# CLUSTER GENERALIZATION OF THE KORRINGA - KOHN - ROSTOKER COHERENT - POTENTIAL APPROXIMATION FOR DISORDERED ALLOYS

By

SAYED SUHEL ARSHAD RAZEE

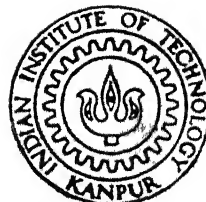**DEPARTMENT OF PHYSICS**

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# CLUSTER GENERALIZATION OF THE KORRINGA - KOHN - ROSTOKER COHERENT - POTENTIAL APPROXIMATION FOR DISORDERED ALLOYS

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in Partial Fulfilment of the Requirements
for the Degree of
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By

SAYED SUHEL ARSHAD RAZEE

*to the*

**DEPARTMENT OF PHYSICS**

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# CERTIFICATE

It is certified that the work contained in the thesis entitled Cluster generalization of the Korringa-Kohn-Rostoker coherent-potential approximation for disordered alloys, by Sayed Suhel Arshad Razee, has been carried out under my supervision, and that this work has not been submitted elsewhere for a degree.

R. Prasad

(Dr. Rajendra Prasad)

Department of Physics,

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February, 1991

*(Allah) Taught man that*
*Which he knew not.*

Al-Qur'an (96:5)

To my
Late Dadiamman,
Mrs. Durr-e-Yaqoot

# SYNOPSIS

The Korringa-Kohn-Rostoker coherent-potential
approximation (KKR-CPA) is a first-principles parameter-free
theory for the electronic structure calculation of purely
random disordered alloys within the local density
approximation of the density functional theory. The KKR-CPA
is a mean-field theory, in which the random disordered medium
is replaced by a translationally symmetric effective medium
with an effective scatterer on each site of the lattice. The
strength of the effective scatterer is determined by a
self-consistency condition that the average extra scattering
(with respect to the medium) from a real atom embedded in the
effective medium be zero. It has been found that the KKR-CPA
provides a reliable description of the electronic properties
of the random alloys. However, the KKR-CPA is a single-site
approximation, in which the statistical correlations between
the configuration fluctuations at a given site and the rest
of the medium are not taken into account. In other words,
the correlated scattering between two or more sites is
neglected. Therefore, it is likely to fail whenever a
single-site effective medium description of the system is not
adequate, e.g. in presence of strong local environmental
effects, such as the short-range order and clustering

tendencies. The local environmental effects give rise to
sharp structures in the density of states, which may strongly
influence the physical properties, like the formation of the
magnetic moments, the Fermi energy, the density of states at
the Fermi energy, the electronic specific heat etc. Since
these local environmental effects involve correlations among
many sites, they can be investigated accurately and
convincingly, only within a multisite or cluster theory.
This underlines the need for the cluster generalization of
the KKR-CPA theory.

The primary aim of this thesis is to present a first-
principles parameter-free cluster generalization of the
KKR-CPA theory, within the local density approximation of the
density functional theory. We have developed this cluster
generalization by combining the augmented space formalism and
the conventional KKR Green's function formulation of the
disordered alloys. The augmented space formalism was
originally developed in the tight-binding framework, and it
provides a self-consistent cluster coherent-potential
approximation (CCPA). This CCPA preserves the analytic
properties (herglotz properties) of the averaged Green's
function (Chapter 2), and therefore, guarantees a
single-valued, continuous and non-negative density of states
at all energies. It also restores the translational
invariance of the effective medium. These are the striking

features of our CCPA, which all other self-consistent cluster approaches, with a few exceptions, fail to maintain, and therefore, yield unphysical results. The ideas of the augmented space formalism are rather general and can be used for muffin-tin models as well. We have been able to effectively combine the augmented space formalism and the conventional KKR method to develop the KKR-CCPA theory.

In Chapter 2, we present a brief account of the augmented space formalism and discuss the unique way in which the configuration averaging is handled. The basic philosophy behind the CCPA and the procedure leading to it, are briefly outlined. One of the achievements of the present work is the proof of analyticity of the augmented space CCPA. We prove three theorems regarding the analyticity of the configuration averaged Green's function. It is shown that the CCPA yields an averaged Green's function which is herglotz and that, the iteration scheme for self-energy always converges to a unique, herglotz and bounded value, provided one starts off with a bounded and herglotz initial guess.

In Chapter 3, we present the KKR-CCPA formulation. This formulation is valid for purely random systems and does not take into account the non-random effects like short-range order. Although, in the KKR method there is no off-diagonal disorder, the KKR-CCPA, quite predictably, introduces off-diagonal corrections as well in the scattering matrices,

along with the usual diagonal corrections. A formula for the configuration averaged Green's function within the KKR-CCPA is derived from which various electronic properties, such as the density of states (total, component, and l-decomposed) and the charge densities (total and component) can be calculated. The component charge densities are essential for a full charge self-consistent implementation of the KKR-CCPA within the local density approximation of the density functional theory. This makes our KKR-CCPA, a first-principles parameter-free cluster generalization of the KKR-CPA theory of disordered alloys. The problem of embedding a cluster of impurities in the KKR-CCPA medium is also discussed in detail. The calculation of local densities of states on these impurities is helpful in understanding the structures in the density of states calculated within the KKR-CCPA.

Chapter 4 deals with the application of the KKR-CCPA formulation to a simple model, a muffin-tin alloy in one dimension. A one-dimensional muffin-tin alloy retains many of the features of its three-dimensional counterpart, while greatly reducing the computational effort. Therefore, it presents itself as an ideal model for testing the KKR-CCPA theory. We have calculated the density of states for this model and found that the KKR-CCPA produces sharp structures in the density of states in contrast to somewhat smooth

representation in the KKR-CPA. We have been able to correlate the sharp structures in the KKR-CCPA density of states with those in the local density of states on the impurities embedded in the KKR-CPA medium. Therefore, we conclude that the structures in the KKR-CCPA density of states are due to the correlated scattering from two or more sites.

The KKR-CCPA formulation presented in Chapter 3 is valid for purely random alloys. However, in reality, almost all the disordered alloys exhibit a certain degree of short-range order. In Chapter 5, we present a formal extension of the KKR-CCPA theory to include the effects of short-range order. This theory reduces exactly to the KKR-CCPA formulation for random alloys (Chapter 3), in the limit of no short-range order. In this formulation, the configuration averaged Green's function in presence of short-range order is expanded about that of a random system. This expansion contains an infinite number of terms. To make the theory computationally feasible, we used an approximation, in which we neglected the higher order terms in the expansion. This approximation was earlier suggested by Gray and Kaplan [Phys. Rev. B 24, 1872 (1981)], in the context of a tight-binding model. We have applied this formulation to calculate the density of states for the one-dimensional model presented in Chapter 4. It is found that, the density of states remains positive throughout

the whole energy range, for a reasonably wide range of
short-range order parameter. It becomes negative at some
points, only in the strong short-range order regime. This is
because we have neglected the higher order terms in the
expansion of the Green's function, which may be important in
this regime. Our results are consistent with the results of
Gray and Kaplan, who used a similar formulation for a
tight-binding model.

In Chapter 6, we summarize the main conclusions and
discuss the achievements, shortcomings, and limitations of
the present work. Also, we suggest the scope of future work
in this direction.

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I take this opportunity to pay homage to my beloved grand mother, Mrs. Durr-e-Yaqoot, who expired on January 29, 1991. May Allah grant peace to her soul (Amen).

No words can truly express my feeling of gratitude to my parents, whom I fondly call Abujaan and Mummy. It were they who encouraged me to take a career in physics.

Sayed Suhel Arshad Razee

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# CHAPTER 1
## INTRODUCTION

The disordered alloys are an indispensable part of most of the present day technological and scientific developments taking place around us. Their technological potential can be fully exploited if we understand the diverse physical and chemical properties of these materials. The electrical, magnetic, transport, thermal, optical and superconducting properties, the phase formation and the stability of the disordered alloys are few examples of such properties. Due to their technological importance, the disordered alloys have, since long, been an important research topic in experimental physics. The theoretical understanding of these alloys offers a great intellectual challenge. Most of the current theoretical studies on disordered alloys are being devoted to the simplest kind of disordered alloys, namely, the substitutionally disordered alloys. In such alloys, there exists a lattice structure, but each lattice point can be occupied by either of the constituent atoms with certain probabilities, which depend upon the concentrations of the constituents as well as on the local environment of the site. In this thesis, we will focus only on the substitutionally disordered alloys.

The disordered alloys lack the translational symmetry or the periodicity, and therefore, Bloch's theorem is not applicable to these systems. With the violation of the Bloch's theorem the entire edifice of elegant theories built around it crumbles. This difficulty has been eliminated with the development of sophisticated scattering theories and the use of Green's functions. The difficulty arising due to the loss of periodicity is overcome by introducing mean-field theories. In a mean-field approach, the disordered medium is replaced by a translationally symmetric effective medium with an effective atom on each site of the lattice. Since the effective medium is periodic, we can use the existing tools for a periodic solid to calculate the properties of disordered alloys.

To understand, how to define the effective medium, let us consider the problem of interpretation and comparison of properties calculated for the effective medium with the experimentally determined results. In an experiment, one measures the properties of different samples of the same material. In a disordered alloy, the spatial arrangement of atoms, in general, varies from sample to sample. Each such arrangement is called a configuration or an ensemble. It is thus obvious, that different samples of an alloy correspond to different configurations. When we talk about the characteristics of the samples we measure, we mean an average

trend among the different samples, and we are not interested in the variations between the samples. Therefore, the experimental characteristics of a material is an average characteristics of different samples or different configurations. For this reason, it is the configuration averaged quantity, determined theoretically, which should be compared with the experimentally determined characteristics. Therefore, the effective medium should be such that the effective medium properties are the same as the configuration averaged properties of the alloy. This is the philosophy behind all the mean-field approximations. A host of mean-field approximations have been proposed for disordered alloys, such as the virtual crystal approximation[1], the average t-matrix approximation[2], the coherent potential approximation[3-5] (CPA) etc.

The current studies on the substitutionally disordered alloys are mostly being done within the CPA.[6-8] The CPA is a mean-field theory for purely random alloys, and is a single-site approximation. In the CPA, the real disordered system is replaced by a translationally symmetric effective medium with an effective scatterer on each site of the lattice. The strength of the effective scatterer is determined through a self-consistency condition, which requires that the average extra scattering with respect to the medium, from a single real atom embedded in the effective

medium be zero. It is generally agreed that the CPA is the best single-site approximation.[6] It preserves the analytic properties of the Green's function,[9,10] and has been applied very successfully to calculate the electronic density of states[5-8] and transport properties[11] of a wide variety of disordered alloys. When the CPA is used for a Hamiltonian with non-overlapping muffin-tin potentials, the theory is called the Korringa-Kohn-Rostoker coherent-potential approximation[7,8,12] (KKR-CPA). The KKR-CPA theory provides a reliable, first-principles parameter-free description of the electronic properties of disordered alloys within the local density approximation[13] of the density functional theory.[14,15] In the CPA, like all other single-site approximations, the statistical correlations between the configuration fluctuations at a given site and the rest of the medium are neglected. Therefore, the CPA is likely to fail whenever a single-site effective medium description becomes inadequate, e.g. in presence of strong local environmental effects, such as short range order and clustering tendencies. The fluctuations in the local environment of a site are responsible for sharp structures in the density of states, which may strongly influence some physical properties, such as the formation of magnetic moments, the Fermi energy, the density of states at the Fermi energy, the electronic specific heat etc. An illustrative

example is the magnetic behavior of the CuNi alloy. It is well-known that Ni atoms will carry a magnetic moment only if surrounded by a sufficiently large number of other Ni atoms.[16,17] Also, the experimental value of the critical concentration of Ni below which the alloy no longer remains magnetic[18-20] (~ 47 %) does not match with the theoretical predictions based on the CPA.[18] In addition, many of the disordered alloys are known to exhibit short-range order, e.g. CuPd (Ref. 21) and CuPt (Ref. 22) systems. It has been found that, the density of states of CuPd alloys calculated within the KKR-CPA[23,24] does not compare favorably with experimental results.[25,26] The disagreement between the experimental and calculated results may be due to the single-site nature of the KKR-CPA theory, in which local environmental effects are not taken into account.[27] These local environmental effects, which involve correlations among many sites, can be investigated accurately and convincingly, only within the context of a cluster or multisite theory.

The need to go beyond the CPA was realized almost immediately after the introduction of the CPA, and since then, several attempts have been reported towards such a generalization. In the beginning, all attempts towards cluster generalization of the CPA were made in connection with the tight-binding Hamiltonians,[28-50] because they are easy to handle computationally. These approaches can be

broadly classified into two categories: self-consistent approaches[28-46] and non-self-consistent approaches.[47-50] Most of the earlier attempts were to develop a self-consistent cluster generalization of the CPA. The n-site CPA or CPA(n) of Nickel and Krumhansl,[29] is a diagrammatic approach, in which the scattering by all the pairs of sites is taken into account. Similar approaches have also been reported by several other workers.[30-32] Nickel and Butler[51] discovered through numerical computations that these approaches fail to preserve the analytic properties of the configuration averaged Green's function, and therefore, lack proper physical behavior, i.e. they give negative, discontinuous, and multi-valued density of states in some energy regions. The molecular coherent-potential approximation[28] (MCPA), the travelling cluster approximation[45] (TCA), and the cluster coherent-potential approximation[46] (CCPA) developed in the augmented space formalism[52-55] are the only approaches, which have been proved to be analytic, while preserving the conservation laws and fundamental sum rules.[56-58] In these approaches, no attempt is made to take into account the scattering by all pairs (or triplets). Instead, the statistical correlations are assumed to have a finite range, i.e. upto the sites within some chosen cluster, and scattering by the sites inside the cluster is treated exactly.[54,55,58]

In the MCPA[28] the disordered medium is considered to be
a collection of disconnected clusters (or molecules) chosen
so that the entire lattice can be generated by the
translation of the points in a cluster. The cluster Green's
function becomes a matrix and the scalar CPA self-consistency
condition is generalized to a matrix self-consistency
condition. The effective medium produced by the MCPA is not
translationally invariant. In addition, the MCPA is very
difficult to implement computationally, becoming impractical
even for nearest-neighbor clusters in three-dimensional
systems. Some authors[36-43] tried to circumvent this
difficulty by imposing further approximations on top of the
MCPA. The idea was to neglect the off-diagonal matrix
elements of the self-energy completely, thereby making it
site-diagonal. The self-consistency is imposed only on
certain diagonal elements of the Green's functions. Then the
theory depends only on a single parameter, the site-diagonal
element of the self-energy.[43] It is clear that this is an *ad
hoc* prescription, but it simplifies the problem to a great
extent, because, the matrix self-consistency condition of
MCPA can now be cast into a single scalar self-consistent
equation. The self-consistent central-site approximation[38]
was first proposed by Butler and later was used by several
other workers.[39-41] In this approximation, the
self-consistency is imposed between the diagonal element of

the averaged Green's function at the center of the cluster, and a diagonal element of the Green's function of the effective medium. This is quite unphysical, because, once the self-energy is made diagonal, the Green's function at the center of the cluster is almost independent of the external medium,[43] and therefore, it can not be consistent with that of the effective medium. Therefore, it is not surprising that, the central-site approximation shows non-analytic behavior.[51] This difficulty is removed in self-consistent boundary-site approximation,[43] in which the self-consistency is required between a diagonal element of the averaged Green's function at a site on the boundary of the cluster, and a diagonal element of the Green's function of the effective medium. The boundary-site approximation is certainly an improvement on the central-site approximation, because a site at the boundary of the cluster is in intimate contact with the effective medium, and therefore, the Green's function at a boundary-site will depend on the effective medium, and so making it consistent with that of the effective medium is reasonable. The boundary-site approximation yields non-negative density of states, but its analyticity has not been proved. Moreover, it is an *ad hoc* prescription and has not been applied to three dimensional systems.

The TCA[45,57] preserves the translational invariance of the effective medium, but is a very difficult theory. It is derived through a diagrammatic approach. In this case, the chosen cluster travels throughout the lattice, but the correlated scattering at a given instant is restricted to the sites within the cluster. When the cluster-size is increased beyond two sites, the diagrammatic analysis becomes unmanageable. Also, it is very difficult to implement computationally. To our knowledge, it has not been applied to any realistic system yet.

It is now clear that the self-consistent approaches which we discussed in the above, are either too difficult to implement computationally, or they lack proper physical behavior. Therefore, some attempts were made towards non-self-consistent generalization as well. The embedded cluster method of Gonis and Garland,[47] was the first attempt in this direction. In this work, a cluster consisting of a central site and its shell of nearest neighbors is embedded in an effective medium, which is determined within the CPA. The density of states is then obtained from the site-diagonal element of the Green's function at the center of the cluster. The effective medium, however, is not determined self-consistently with respect to the cluster. Gonis and Freeman[50] have proposed a similar technique to include the effects of short-range order.

The tight-binding Hamiltonians possess severe limitations. Various physical quantities that enter into the calculation, e.g. the band centers and the band-widths, are determined from a parameterization procedure. Moreover, when the band-widths of the different constituents of the alloy are different, a tight-binding description requires the introduction of off-diagonal disorder as well. The parameters that describe off-diagonal disorder can be determined only by means of over-simplified interpolation schemes. Such limitations are removed when the system is described by a muffin-tin Hamiltonian. This realization encouraged a few attempts towards the cluster generalization of the CPA for muffin-tin Hamiltonians,[59-62] and this is the main subject of this thesis. The work of Gonis $et$ $al$[59,60], until recently was the only cluster approach in the conventional KKR formulation for disordered alloys. This work[59,60] is basically an extension of the work on tight-binding Hamiltonians by Gonis and Garland.[47] In this work, a cluster consisting of a central site and its shell of nearest neighbors is embedded in an effective medium determined within the KKR-CPA method. The density of states is then obtained from the site-diagonal element of the Green's function at the center of the cluster. In this case also, the effective medium is not determined self-consistently with respect to the cluster. It was then

expected that the effects of lack of cluster self-consistency would be small. However, Stefanou *et al*[27] have shown that, at least for CuPd systems, the effects of cluster self-consistency might be significant.

The primary aim of this thesis is to present a first-principles parameter-free self-consistent cluster generalization of the KKR-CPA formulation, within the local density approximation of the density functional theory.[13-15] Before embarking upon the cluster generalization, let us summarize the requirements for a theory to give physically acceptable results. These are as follows:

(i) The theory must yield analytic, physically meaningful results i.e. it must give single-valued and non-negative density of states and momentum spectral densities. Analyticity is necessary for the fundamental sum rules to be satisfied. The analyticity can be assured by requiring that the configuration averaged Green's function and the self-energy be herglotz functions.[63] A complex operator function $F(z)$ is said to be herglotz if it satisfies the following set of properties:

(a) $F(z)$ is an analytic function of $z$ in the entire cut plane Im $z \neq 0$. Its spectrum is bounded and $F(z)$ behaves like $1/z$ as $z \longrightarrow \pm \infty$.

(b)     $F(z^*) = F^\dagger(z),$                                          (1.1)

where $F^\dagger(z)$ is the hermitian adjoint  of $F(z)$, and

(c)   Im $F(z) \leq 0,$   for Im $z > 0.$                          (1.2)

The imaginary part of an  operator function is  defined as

$$\text{Im } F(z) = (F(z) - F^\dagger(z))/2i \tag{1.3}$$

(ii) The theory should preserve the  symmetries  of  the underlying lattice i.e. the effective  medium  should  be translationally invariant.   This  is  essential  for   the calculation of meaningful momentum spectral densities.

(iii) It should be applicable to general multi-component alloys.

(iv) It should incorporate multisite correlation effects for random as well as non-random alloys.

(v) It should be computationally feasible.

(vi) It should become exact in the weak  scattering  and dilute alloy limits.

(vii) It should incorporate various kinds  of  disorder, such as disorder in the  diagonal  as  well  as  off-diagonal

elements of the alloy Hamiltonian in a tight-binding description.

(viii) It should produce density of states which becomes exact as the cluster size increases.

(ix) It should allow the calculation of one- and two-particle properties in essentially the same formalism.

We have used the augmented space formalism[52-54] to develop the cluster generalization of the KKR-CPA theory. The augmented space formalism is a method of configuration averaging a function of a set of random variables. It was originally developed in the tight-binding framework. It provides a self-consistent approximation, the CCPA[46,54,58], which is a much simpler theory, compared to MCPA[28] and TCA,[45] and is a systematic way of going beyond the CPA. In this method, the disordered medium in real Hilbert space is transformed to a larger Hilbert space, called the augmented space, and the CCPA introduced therein. In the CCPA, the effective medium is determined by the self-consistency requirement that the extra scattering (with respect to the medium) from a real cluster embedded in the medium, averaged over all the possible configurations of the cluster, be zero. The difference between the augmented space CCPA and other cluster approaches lies in the sequence of averaging and approximation procedures. In the augmented space CCPA, the

averaging precedes the approximation, while in the other methods, averaging is done after the approximation. The exact nature and the philosophy of the augmented space CCPA will be discussed in detail in Chapter 2 (section 2.4). This CCPA gives a translationally invariant effective medium, and yields a herglotz approximated averaged Green's function.[58] Also, the self-consistent equations for self-energy always converge to a unique, herglotz, and bounded value, provided we start off with a bounded and herglotz initial guess.[58] This guarantees a unique and non-negative density of states at all energies. The augmented space CCPA has been used extensively for electronic structure calculations in the tight-binding framework.[46,54]

The ideas of the augmented space formalism are rather general, and can be incorporated within the conventional first-principles KKR methods as well.[64] In the KKR method, unlike the tight-binding method, there is no off-diagonal disorder. Therefore, the application of the augmented space formalism to the KKR method is mathematically much simpler than its application to the tight-binding method. However, computationally, the KKR method would be much more demanding. The works of Mookerjee[64] and Rajput *et al*[65] were the first attempts towards incorporation of the CCPA within the KKR method. In these works, an expression for the averaged density of states using Lloyd's formula[6,12] was developed.

This formulation has several limitations. Firstly, it has been observed that, use of Lloyd's formula to calculate certain electronic properties of alloys, such as component densities of states, l-decomposed densities of states, and Bloch spectral density functions is not appropriate, even in the CPA.[12,66] These quantities become negative in certain energy ranges, if calculated using the Lloyd's formula. It is now generally acknowledged that these quantities should be calculated by the Green's function method only.[12] Secondly, the Lloyd's formula does not allow the calculation of charge densities. The component charge densities are essential for full charge self-consistent calculations within the local density approximation of the density functional theory. The charge densities can be calculated only by the Green's function formalism.[12]

In the present thesis, we present a self-consistent field KKR-CCPA formulation[67] for disordered alloys, which has been developed by effectively combining the augmented space formalism and the conventional KKR Green's function formulation. The KKR-CCPA yields a translationally invariant effective medium. However, unlike the KKR-CPA medium, in the KKR-CCPA, the effective scatterers are no longer site-diagonal. The KKR-CCPA, as expected, introduces site-off-diagonal corrections as well, along with the usual site-diagonal corrections in the scattering matrices. Since

the theory attempts to calculate the configuration averaged
Green's function, it allows the calculation of the charge
densities, and therefore, in this theory, one can achieve
charge self-consistency[67] within the local density
approximation of the density functional theory. Thus, the
KKR-CCPA formulation presented in this thesis, is a
first-principles parameter-free theory of disordered alloys.
The most important feature of this theory is its
computational feasibility. The KKR-CCPA self-consistent
equations are presented in such a form, that one has to deal
with the matrices of rank $(l+1)^2$ only, where $l$ is the maximum
number of angular momentum states used in evaluating the
phase-shifts. For most practical purposes, $l = 2$ is quite
satisfactory for d-band metals, which means that, one has to
deal with (9x9) matrices. Therefore, solving KKR-CCPA
equations on modern computers will not be difficult at all.
The work presented in Ref. 67 deals with purely random binary
alloys. However, the extension of this theory to general
multi-component alloys is straightforward.[68]

We have applied the KKR-CCPA formulation to a simple
model, a muffin-tin alloy in one dimension. A
one-dimensional muffin-tin alloy retains many of the features
of its three-dimensional counterpart, while greatly reducing
the computational effort, because the involved $k$-space
integrations are evaluated analytically.[69] Thus, it is an

ideal model to test our theory. We have calculated the density of states for this model using the KKR-CCPA. We observed a few sharp structures in the KKR-CCPA density of states in contrast to a nearly smooth KKR-CPA density of states. It is found that the sharp structures in the KKR-CCPA density of states are due to correlated scattering from clusters of atoms.

The KKR-CCPA formulation (Chapter 3) is valid for purely random alloys. However, in reality, almost all the disordered alloys exhibit a certain degree of short-range order. In Chapter 5, we present a formal extension of the KKR-CCPA theory to include the effects of short-range order. This theory reduces exactly to the KKR-CCPA formulation for random alloys (Chapter 3), in the limit of no short-range order. In this formulation, the configuration averaged Green's function in presence of short-range order is expanded about that of a purely random system. This expansion contains an infinite number of terms. To make the theory computationally feasible, we have used an approximation, in which we keep only the first correction term in the expansion. This approximation was earlier suggested by Gray and Kaplan,[70] in the context of a tight-binding model. This approximation is in addition to the CCPA. We have applied this formulation to calculate the density of states for a one-dimensional muffin-tin alloy. It is found that, the

density of states remains non-negative throughout the whole energy range, for a fairly wide range of short-range order parameter. The density of states becomes negative at some energy points, only when the short-range order is very strong. The unphysical behavior in the strong short-range order regime, is probably due to the breakdown of the approximation, in which the higher order corrections are neglected.

The outline of the thesis is as follows. In Chapter 2, we give a brief account of the augmented space formalism. In section 2.2 we derive the augmented space theorem, which gives the formula for the configuration average of a function of a set of random variables. In section 2.3, we discuss some of the aspects of the disordered alloys, and show how the augmented space theorem can be a useful tool in determining the physical properties of these systems. Due to the large dimensionality of the augmented space for these systems, it is not possible to use the augmented space theorem directly for computational purposes, and one has to resort to some approximations. We have adopted a mean-field approximation, the CCPA, which is presented in section 2.4. The CCPA yields an approximated averaged Green's function, which is herglotz. In section 2.5, we prove three theorems in regards to the analyticity of the approximated averaged Green's function obtained within the CCPA. We prove that,

the self-consistent iteration scheme for the self-energy always converges to a unique, bounded, and herglotz value, provided we start off with a bounded and herglotz initial guess. This guarantees that the averaged Green's function must also be herglotz. In section 2.6, while concluding the discussion, we outline the merits and shortcomings of the augmented space formalism and the CCPA.

Chapter 3 presents the main subject of the work presented in this thesis, i.e. the KKR-CCPA. The KKR-CCPA is the product of an effective combination of conventional KKR Green's function method and the augmented space CCPA. In section 3.2, we present a brief review of the KKR Green's function method. Various equations in this section are presented in a form that lend themselves quite naturally for cluster generalization, presented in section 3.3. In section 3.4, we derive the formula for the configuration averaged Green's function within the KKR-CCPA. Also, in this section, we show how various electronic properties of the alloy, such as the density of states and the charge densities, can be calculated. In section 3.5, the problem of embedding a cluster of real impurities in the KKR-CCPA effective medium and the determination of local properties are discussed. In section 3.6 we make the concluding remarks about contents of Chapter 3.

Chapter 4 deals with the application of the KKR-CCPA theory to calculate the electronic properties of a

one-dimensional muffin-tin alloy. We describe the one-dimensional muffin-tin alloy model in section 4.2. We have implemented the KKR-CCPA on this model for a two-atom cluster. The KKR-CCPA equations for one- and two-atom clusters are presented in section 4.3. The KKR-CCPA equation for a one-atom cluster quite predictably reduces exactly to the familiar KKR-CPA equation. In section 4.4, we present the results of our calculations and their inferences. In section 4.5 we give the conclusions.

In Chapter 5, we present the formal extension of the KKR-CCPA theory for the systems having short-range order. In section 5.2, we discuss some mathematical preliminaries, which we will need in subsequent discussions. In section 5.3, we derive an expression for the configuration averaged Green's function for the systems having short-range order. When the short-range order is limitted to nearest neighbor atoms only, it is called a Markovian type short-range order. We describe a Markov chain in section 5.4. In section 5.5, we present our results. While concluding in section 5.6, we enlist the shortcomings and the limitations of this formalism.

Finally, in Chapter 6, we present our conclusions. In this chapter, the achievements, shortcomings, and the limitations of the present work are discussed. We also discuss the scope of future work on the subject.

# CHAPTER 2
# THE AUGMENTED SPACE FORMALISM

## 2.1 INTRODUCTION

In Chapter 1, we have highlighted the need of
configuration averaging in the study of the properties of
disordered alloys. The augmented space formalism[52-55] is an
straightforward and convenient method to determine the
configuration averaged properties of disordered systems.
This approach centers around a new technique for
configuration averaging a function of independent random
variables. The essential feature of this approach is the
unique way, in which the configuration averages are handled.
The random problem in the real Hilbert space is transformed
into a large new Hilbert space, called the augmented space.
The augmented space is a direct product of the real Hilbert
space and the configuration space, which describes the
configurations of the system. Thus, the augmented space
contains all the informations about the real disordered
system as well as its possible configurations. Therefore,
the configuration averaging is not a further extra process,
as in other effective medium approaches.

A particular configuration of the disordered system can be described by a sequence of random occupation variables $\{n_i\}$ in a particular order. A certain probability density $\mathcal{P}(\{n_i\})$ is associated with a particular configuration. Let us consider a physical observable $A(\{n_i\})$ of that particular configuration. By definition, the configuration average of $A(\{n_i\})$ is given by

$$\langle A(\{n_i\}) \rangle = \int A(\{n_i\}) \; \mathcal{P}(\{n_i\}) \; \prod_i dn_i \; . \tag{2.1}$$

We begin with the simplification that various $n_i$'s are statistically independent. This condition corresponds to a purely random system, and is not valid for disordered alloys with short-range order. A formal extension of the theory to include the effect of short-range order in disordered alloys will be presented in Chapter 5. In the present case, the composite probability density $\mathcal{P}(\{n_i\})$ can be decomposed into a product of probability densities of individual random variables,[52] i.e.

$$\mathcal{P}(\{n_i\}) = \prod_i P_i(n_i) . \tag{2.2}$$

Now Eq. (2.1) can be written as

$$\langle A(\{n_i\}) \rangle = \int A(\{n_i\}) \prod_i P_i(n_i) \, dn_i \quad .$$

(2.3)

In section 2.2, we will show that this integral can be evaluated exactly by the augmented space formalism.

The outline of this chapter is as follows. In section 2.2, we derive the augmented space theorem, which in effect is a formula for the configuration average of a function of a set of random variables. This is applicable to any random disordered system. In section 2.3, we briefly describe the usefulness of the augmented space theorem in calculating the configuration averaged properties of disordered alloys. In section 2.4, we present the cluster coherent-potential approximation (CCPA) for a tight-binding Hamiltonian. The CCPA is a generalized mean-field approximation, but the nature and philosophy of this approximation is distinctly different from other mean-field approximations based on the embedding of a cluster in the effective medium. The exact nature of the CCPA is also discussed in this section. In section 2.5, we prove three theorems regarding the analytic properties of the augmented space CCPA. We show that the configuration averaged Green's function and the self-energy obtained by this approximation, are herglotz. This

guarantees a single-valued and non-negative density of states. In section 2.6, we enlist the achievements and shortcomings of the method.

## 2.2 THE AUGMENTED SPACE THEOREM

The basic idea behind the augmented space formalism originated from the recursion method of Haydock.[71] The recursion method can be summarized in the following few lines. A self-adjoint Hamiltonian in a given basis can be transformed into a tri-diagonal Hamiltonian in some new basis. Then the local density of states, related to the Hamiltonian $H$ as

$$\rho_i(E) = - \frac{1}{\pi} \, \text{Im} \, \langle \, i | \, (E \, I - H \,)^{-1} | i \, \rangle \qquad (2.4)$$

can be expressed as a continued fraction expansion as

$$\rho_i(E) = - \frac{1}{\pi} \, \text{Im} \, \cfrac{1}{E - \alpha_1 - \cfrac{\beta_1^2}{E - \alpha_2 - \cfrac{\beta_2^2}{\ddots}}} \qquad (2.5)$$

with $\alpha_n$ down the diagonal and $\beta_n$ down the off-diagonal positions of the new tri-diagonal Hamiltonian. The local density of states has the following properties,

$$\rho_i(E) \geq 0,$$

and (2.6)

$$\int \rho_i(E) \, dE \quad \text{is finite.}$$

Now we note that the probability density $P_i(n_i)$ shares with the density of states, the following properties,

$$P_i(n_i) \geq 0,$$

and (2.7)

$$\int P_i(n_i) \, dn_i = 1 \quad \text{(finite).}$$

This suggests that the probability density $P_i(n_i)$ could be expressed as the imaginary part of a herglotz function and can be written as a continued fraction expansion,[72] i.e.

$$P_i(n_i) = -\frac{1}{\pi} \, \text{Im} \cfrac{1}{n_i - \alpha_1 - \cfrac{\beta_1^2}{n_i - \alpha_2 - \cfrac{\beta_2^2}{\ddots}}} \qquad (2.8)$$

By the inverse process from Eq. (2.5) to Eq. (2.4), $P_i(n_i)$ can be represented as a matrix element of the resolvent of a self-adjoint operator $M^i$ (Ref. 52), i.e.

$$P_i(n_i) = -\frac{1}{\pi} \, \text{Im} \langle \nu_0^i | (n_i I - M^i)^{-1} | \nu_0^i \rangle. \qquad (2.9)$$

Here, $M^i$ is a tri-diagonal matrix in the configuration space $\phi_i$ spanned by $\{|\nu_j^i\rangle\}$, j= 0, 1, ...(m-1), where m is the number of possible values $n_i$ can take. Thus, cardinality of the basis $\{|\nu_j^i\rangle\}$ is (m-1). The state $|\nu_0^i\rangle$ is called the ground configuration state and it is defined such that the matrix element $\langle \nu_0^i| M^i |\nu_0^i\rangle$ is the first coefficient $(\alpha_1)$ in the continued fraction expansion in Eq. (2.8). We may mention that the operator $M^i$ may not be unique. However, the non-uniqueness of $M^i$ does not pose any problem in the mathematical formulation of the problem. The point, which does matter is, whether the continued fraction expansion in Eq. (2.8) contains finite number of terms, that is to say, whether the operator $M^i$ is of a finite rank. This can be assured, if we assume that $P_i(n_i)$ has finite moments to all orders[72] i.e.

$$\int P_i(n_i) \, n_i^{\ell} \, dn_i \quad \text{is finite} \quad \text{for } \ell = 0,1,2,\ldots \quad (2.10)$$

This condition is satisfied by almost all the physically valid probability distributions, the only exception being the Lorentzian distribution.[52]

With the help of Eq. (2.9), we can rewrite Eq. (2.3) as

$$\langle A \rangle = \int A(\{n_i\}) \left[ \prod_i \left\{ -\frac{1}{\pi} \text{Im} \langle \nu_0^i | (n_i I - M^i)^{-1} | \nu_0^i \rangle \, dn_i \right\} \right].$$

(2.11)

We can evaluate this integral by integrating out one variable at a time. Let us first integrate out the j-th variable and call it $\mathcal{I}_j$

$$\mathcal{I}_j = \int A(\{n_i\}) \left[ -\frac{1}{\pi} \text{Im} \langle \nu_0^j | (n_j I - M^j)^{-1} | \nu_0^j \rangle \right] dn_j \, .$$ (2.12)

Let $|\mu^j\rangle$ be the eigenvectors of $M^j$ with eigenvalues $\mu^j$ i.e.

$$M^j |\mu^j\rangle = \mu^j |\mu^j\rangle.$$

(2.13)

Then, the completeness condition is

$$\sum_{\mu^j} |\mu^j\rangle\langle\mu^j| = 1,$$

and

(2.14)

$$\langle \mu_1^j | \mu_2^j \rangle = \delta_{12} \, .$$

Rewriting Eq. (2.12) as

$$\mathscr{G}_j = \langle \nu_0^j | \int A(\{n_i\}) \left[ -\frac{1}{\pi} \operatorname{Im} \left\{ \sum_{\mu_1^j} \sum_{\mu_2^j} |\mu_1^j\rangle\langle\mu_1^j| \right. \right.$$

$$\left. \left. (n_j I - M^j)^{-1} |\mu_2^j\rangle\langle\mu_2^j| \right\} \right] dn_j \; |\nu_0^j\rangle$$

$$= \langle \nu_0^j | \int A(\{n_i\}) \left[ -\frac{\operatorname{Im}}{\pi} \sum_{\mu_1^j} \sum_{\mu_2^j} |\mu_1^j\rangle \frac{\delta_{12}}{(n_j - \mu_1^j)} \langle\mu_2^j| \right] dn_j |\nu_0^j\rangle$$

$$= \langle \nu_0^j | \int A(\{n_i\}) \left[ -\frac{\operatorname{Im}}{\pi} \sum_{\mu^j} |\mu^j\rangle \frac{1}{(n_j - \mu_1^j)} \langle\mu^j| \right] dn_j |\nu_0^j\rangle .$$

$$(2.15)$$

We now use the identity

$$-\frac{1}{\pi} \operatorname{Im} \frac{1}{x + i0 - a} = \delta(x - a) \qquad (2.16)$$

to get

$$\mathscr{G}_j = \langle \nu_0^j | \int A(\{n_i\}) \left[ \sum_{\mu^j} |\mu^j\rangle \; \delta(n_j - \mu^j)\langle\mu^j| \right] dn_j |\nu_0^j\rangle$$

$$= \langle \nu_0^j | \sum_{\mu^j} |\mu^j\rangle \; A(\{n_i, i \neq j\}, \mu^j) \; \langle\mu^j|\nu_0^j\rangle . \qquad (2.17)$$

And since $|\mu^j\rangle$ are the eigenvectors of $M^j$ we immediately

get

$$\mathcal{G}_j = \langle \nu_0^j | \; \tilde{A}(\{n_i, i \neq j\}, M^j) \; |\nu_0^j\rangle. \qquad (2.18)$$

Note that, $\tilde{A}(\{n_i, i \neq j\}, M^j)$ is the same function of $M^j$ as $A(\{n_i, i \neq j\}, n_j)$ is of $n_j$ (Ref. 52). If we integrate all the variables in the above procedure, after integration, all the $n_j$'s will be replaced by the corresponding $M^j$'s, i.e.

$$\langle A(\{n_i\}) \rangle = \langle f | \; \tilde{A}(\{M^i\}) | f\rangle, \qquad (2.19)$$

where

$$|f\rangle = |\nu_0^1 \; \nu_0^2 \; \nu_0^3 \; \ldots\ldots \; \nu_0^i \; \ldots\ldots\rangle \equiv \prod_i |\nu_0^i\rangle. \qquad (2.20)$$

The state $|f\rangle$ is the ground configuration state in the space $\Phi = \prod_i \phi_i$, which contains the information about all the possible configurations of the system. $\tilde{A}(\{M^i\})$ is an operator functional in the augmented space $\Psi = \mathcal{H} \otimes \Phi$, where $\mathcal{H}$ is the real Hilbert space. $\tilde{A}(\{M^i\})$ is the same function of $\{M^i\}$ as $A(\{n_i\})$ is of $\{n_i\}$. Eq. (2.19) is called the Augmented space theorem.[52,54] A general configuration state spanning $\Phi$ is of the form[58]

$$|f_{\sigma,C}\rangle = |\nu_{m_1}^1 \; \nu_{m_2}^2 \; \nu_{m_3}^3 \; \ldots\ldots \nu_{m_i}^i \; \ldots\ldots\rangle. \qquad (2.21)$$

This state can be uniquely described by the set of points $\sigma = \{j: m_j \neq 0\}$, at which there are excitations, and

the set of cardinalities$^{73}$ $C = \{m_j\}$ at those points. For a binary distribution (as in binary alloys), the cardinality of any excitation is 1 (discussed in detail in the next section) and thus the labelling C may be omitted in this case. In this notation the ground configuration state is $|f\rangle = |\underset{\sim}{f}_{\emptyset}\rangle$, where $\emptyset$ denotes the null set. We shall also write $\langle f_C | Q | f_{C'} \rangle$ as $Q^{CC'}$ for any operator $Q$ in the augmented space. In this notation the augmented space theorem can be written as

$$\langle\langle A(\{n_i\})\rangle\rangle = \left[\ \tilde{A}(\{M^i\})\ \right]^{\emptyset\emptyset}. \tag{2.22}$$

## 2.3 APPLICATION TO DISORDERED ALLOYS

The substitutionally disordered alloys are the simplest kind of disordered systems. In such alloys, if we neglect the correlation between the sites then, each site can be occupied by m different kinds of atoms, for an m-component alloy.

Let us consider an alloy, described by a random tight-binding Hamiltonian,

$$H = \sum_{i} \varepsilon_i \ |i\rangle\langle i| + \sum_{\substack{ij \\ (i\neq j)}} V_{ij} \ |i\rangle\langle j|. \tag{2.23}$$

The states $\{|i\rangle\}$ are Wannier states associated with the sites $\{i\}$. The Green's function of the system is defined as

$$G(z) = (z\,I - H\,)^{-1},$$ (2.24)

where $z$ is a complex number. We will always work on the upper half-plane, $\text{Im } z > 0$, throughout this thesis. Now, Eq. (2.24) can be rewritten as

$$G(z) = \frac{1}{z}\left[\,I - \frac{1}{z}\,H\,\right]^{-1}$$

$$= \frac{1}{z} + \frac{H}{z^2} + \frac{H^2}{z^3} + \cdots\cdots\cdots\cdots$$

$$= \sum_{n=0}^{\infty} \frac{1}{z^{n+1}}\,H^n,$$ (2.25)

so that, any element $G_{ij}(z)$ can be written as

$$G_{ij}(z) = \sum_{n=0}^{\infty} \frac{1}{z^{n+1}}\,\langle i|\,H^n\,|j\rangle$$

$$= \frac{\delta_{ij}}{z} + \frac{H_{ij}}{z^2} + \sum_{k}\frac{H_{ik}H_{kj}}{z^3} + \cdots\cdots\cdots$$ (2.26)

It follows from Eq. (2.26) that, in the plane $\text{Im } z \neq 0$, $G_{ij}(z)$ has no singularity, and therefore, is analytic. The

singularities of $G_{ij}(z)$ are thus restricted to the real axis. Also, from Eq. (2.26) it follows that,

$$G_{ij}(z) \sim \frac{\delta_{ij}}{z} \quad \text{as} \quad z \longrightarrow \pm \infty. \tag{2.27}$$

We can also show, by simple algebra, that,

$$\text{Im } G(z) = - G^{\dagger}(z) \, G(z) \, \text{Im } z, \tag{2.28}$$

which implies that, $\text{Im } G(z) < 0$, for $\text{Im } z > 0$.

Since $H$ is hermitian and bounded, it follows from Eqs. (2.27) and (2.28) that, $G(z)$ satisfies the herglotz properties[63] defined in Chapter 1. The configuration average of Eq. (2.28) gives us

$$\text{Im } \langle G(z) \rangle = - \langle G^{\dagger}(z) \, G(z) \rangle \, \text{Im } z. \tag{2.29}$$

It is evident from Eq. (2.29) that, the averaged Green's function retains the herglotz properties of the exact Green's function. If we define an effective medium, described by a translationally invariant effective Hamiltonian $\Sigma$ (also called the self-energy), then the Green's function for the system is

$$\mathcal{G}(z) = (z \, I - \Sigma)^{-1} \tag{2.30}$$

thus giving

$$\text{Im } \mathcal{G}(z) = - \mathcal{G}(z) \text{ Im } (z \text{ I} - \Sigma) \mathcal{G}^{\dagger}(z). \qquad (2.31)$$

And since $\mathcal{G}(z)$ is herglotz, it immediately follows from Eq. (2.31) that $\Sigma(z)$ also is a herglotz function of $z$.[10,58] Conversely, if $\Sigma(z)$ is herglotz, then $\mathcal{G}(z)$ is also herglotz.

For any approximation to be physically acceptable, the approximated averaged Green's function and the self-energy, must, therefore, be herglotz. In section 2.5, we will show that the CCPA presented in section 2.4, conforms to this criteria.

Let us apply the augmented space theorem to find the configuration averaged Green's function for the system described by the random Hamiltonian of Eq. (2.23). For this purpose we will have to express $H$ as a function of a set of random variables $\{n_i\}$. We consider a binary alloy $A_x B_y$, for which the occupation of a site i can be described by a random variable $n_i$ defined as

$$n_i = \begin{cases} 1, \text{ when site i is occupied by A} \\ 0, \text{ when site i is occupied by B} \end{cases}. \qquad (2.32)$$

The random parameters $\varepsilon_i$ and $V_{ij}$ in Eq. (2.23) can be written in terms of the random variables $\{n_i\}$ as

$$\varepsilon_1 = \varepsilon_B + (\varepsilon_A - \varepsilon_B) \, n_1 \;,$$

and                                                                          (2.33)

$$V_{ij} = V_{BB} + (V_{AA} + V_{BB} - V_{AB} - V_{BA}) \, n_i \, n_j +$$

$$(V_{AB} - V_{BB}) \, n_i + (V_{BA} - V_{BB}) \, n_j \;.$$

Substituting Eq. (2.33) in Eq. (2.23), we get $\mathsf{H}$ as a function of random variables $\{n_i\}$ i.e. $\mathsf{H} \equiv \mathsf{H}(\{n_i\})$, for which the Green's function,

$$G(\{n_i\}) = \left[ z \, I - \mathsf{H}(\{n_i\}) \right]^{-1} \qquad (2.34)$$

is also a random function. The probability density $P_i(n_i)$ can be written as

$$P_i(n_i) = x \, \delta(n_i - 1) + y \, \delta(n_i), \qquad (2.35)$$

which satisfies Eqs. (2.7) and (2.10). Therefore, the continued fraction expansion of $P_i(n_i)$ will converge after a finite number of terms. Using Eq. (2.16) we can rewrite Eq. (2.35) as

$$P_i(n_i) = -\frac{1}{\pi} \, \text{Im} \left[ \frac{x}{n_i - 1} + \frac{y}{n_i} \right]$$

$$= -\frac{1}{\pi} \, \text{Im} \, \frac{1}{n_i - x - \dfrac{xy}{n_i - y}} \, . \qquad (2.36)$$

This shows that the operator $M^i$ for a binary distribution is a tri-diagonal matrix of rank 2 and is given by[54]

$$M^i = \begin{pmatrix} x & (xy)^{1/2} \\ (xy)^{1/2} & y \end{pmatrix}, \qquad (2.37)$$

in a space $\phi_i$ spanned by $|\nu_0^i\rangle$ and $|\nu_1^i\rangle$. It is easily seen that

$$M^i \, |\nu_0^i\rangle = x \, |\nu_0^i\rangle + (xy)^{1/2} \, |\nu_1^i\rangle,$$

and
$$\qquad (2.38)$$

$$M^i \, |\nu_1^i\rangle = y \, |\nu_1^i\rangle + (xy)^{1/2} \, |\nu_0^i\rangle.$$

A general state $|f_\sigma\rangle$ in the total configuration space $\Phi$ can be written as[58]

$$|f_\sigma\rangle = \prod_i |\nu_n^i\rangle \, , \text{ with } n = \begin{cases} 0, \text{ for } i \notin \sigma \\ 1, \text{ for } i \in \sigma \end{cases} \qquad (2.39)$$

Now applying the augmented space theorem to Eq. (2.34) we get

$$\langle G(\{n_i\}) \rangle = \langle f | \left[ z \, I - \tilde{H}(\{M^i\}) \right]^{-1} | f \rangle \qquad (2.40)$$

where $\tilde{H}(\{M^i\})$ is obtained by replacing $\{n_i\}$ in $H(\{n_i\})$ by $\{M^i\}$.

For a ternary system $A_x B_y C_z$, Mookerjee and Thakur[68] have shown that if we define the random variables as

$$n_i = \begin{cases} 1, & \text{when site } i \text{ is occupied by A} \\ 0, & \text{when site } i \text{ is occupied by B} \\ -1, & \text{when site } i \text{ is occupied by C} \end{cases} \qquad (2.41)$$

then the operator $M^i$ is a tri-diagonal matrix of rank 3 with the representation

$$M^i = \begin{bmatrix} \alpha_1 & \beta_1 & 0 \\ \beta_1 & \alpha_2 & \beta_2 \\ 0 & \beta_2 & \alpha_3 \end{bmatrix}, \qquad (2.42)$$

where

$$\alpha_1 = x-z, \qquad \alpha_2 = \delta-(x-z), \qquad \alpha_3 = -\delta$$

$$(2.43)$$

$$\beta_1 = \left[ x+z-(x-z)^2 \right]^{1/2}, \qquad \beta_2 = \left[ y-\delta(\delta-x+z) \right]^{1/2}$$

with

$$\delta = \left[ y(x-z) \right] / \left[ x+z-(x-z)^2 \right].$$

The cardinality of the basis is 2 and the single site configuration spaces $\phi_i$ are spanned by $|\nu_0^i\rangle$, $|\nu_1^i\rangle$, and $|\nu_2^i\rangle$, with $|\nu_0^i\rangle$ as the ground configuration state.

We can determine $M^i$ for any multicomponent alloy if we know the concentrations of the different constituents in the alloy. The dimensionality of the augmented space is $NxM^N$, where M is the number of species and N is the total number of atoms in the alloy. This is quite large for a macroscopic system ($N \sim 10^{23}$), and therefore, Eq. (2.40) can not be used directly to calculate the configuration averaged Green's function. In principle, Eq. (2.40) can be evaluated numerically by using the recursion method, and it has been done for a one-dimensional model in the tight-binding framework.[53] However, for three-dimensional systems, so far no attempt has been made in this direction, because it will be computationally extremely demanding. In practice, one uses the augmented space theorem with some approximation. In the next section, we will discuss the approximation we have used, which we call the CCPA.[54,58]

## 2.4  THE CLUSTER COHERENT-POTENTIAL APPROXIMATION (CCPA)

The CCPA is a mean-field approximation. In this approximation, a finite compact cluster of sites, $\mathbb{C}$ is chosen

out of $\{1\}$ in $\mathcal{H}$, and the complement of the cluster is replaced by an effective medium. It is immaterial which particular set of sites we choose. What is important is the relative position of these sites with respect to one another.[58] The configuration fluctuation is allowed only within the cluster, and therefore, the configuration averaging is done only over the possible configurations of the cluster. The procedure leading to the CCPA involves two steps. In the following, we describe these steps.

Let $\mathfrak{C}$ be the set of all possible vectors in the configuration space, i.e. $\mathfrak{C} = \{|f_{\sigma}\rangle\}$. In the first step, we define a subspace $\Psi_1$ spanned by $\{|i,f_{\sigma}\rangle, i \in \mathbb{C}, f_{\sigma} \in \mathfrak{C}\}$ and its complement in $\Psi$, $\Psi_2 = \Psi\backslash\Psi_1$ . We partition $\Psi$ into these two subspaces, and from Eq. (2.40), by applying the partition theorem of matrices, we get

$$G_1 = \left[z\,I_1 - H_1 - H_{12}\,G_2\,H_{12}^{\dagger}\right]^{-1} = \left[z\,I_1 - \hat{H}\right]^{-1}, \qquad (2.44)$$

where,

$$\hat{H} = H_1 + H_{12}\,G_2\,H_{12}^{\dagger} \qquad (2.45a)$$

$$H_1 = \mathcal{P}_1\,\tilde{H}\,\mathcal{P}_1 , \qquad (2.45b)$$

$$H_2 = \mathcal{P}_2\,\tilde{H}\,\mathcal{P}_2 , \qquad (2.45c)$$

$$H_{12} = \mathcal{P}_1 \tilde{H} \mathcal{P}_2 \; , \tag{2.45d}$$

and,

$$G_2 = \left[ z \, I_2 - H_2 \right]^{-1} . \tag{2.45e}$$

Here $\mathcal{P}_j$ is the projection operator in the subspace $\Psi_j$ , and can be written as,

$$\mathcal{P}_1 = \sum_{i \in \mathbb{C}} \; \sum_{f_\sigma \in \mathbb{S}} | i; f_\sigma \rangle \langle i; f_\sigma | \; ,$$

and, $\tag{2.46}$

$$\mathcal{P}_2 = \sum_{i \notin \mathbb{C}} \; \sum_{f_\sigma \in \mathbb{S}} | i; f_\sigma \rangle \langle i; f_\sigma | \; .$$

If we write

$$\hat{H} = H_1 + \mathfrak{X} \; , \tag{2.47}$$

then we have,

$$\mathfrak{X}^{\sigma \sigma'} = \sum_{\alpha, \alpha'} H_{12}^{\sigma \alpha} \; G_2^{\alpha \alpha'} \; H_{12}^{\dagger \alpha' \sigma'} . \tag{2.48}$$

We shall now introduce the crucial mean-field approximation on $\mathfrak{X}$, in which the subspace $\Psi_2$ is replaced by an effective medium. The effective medium is translationally symmetric and is defined by the self-energy $\sum$, which is the effective Hamiltonian. Due to the absence of randomness in

subspace $\Psi_2$ , there is no configuration fluctuation in it,[58]
and therefore,

$$G_2^{\alpha\alpha'} = G_2(\Sigma) \, \delta^{\alpha\alpha'} ,$$

and

$$H_{12}^{\sigma\alpha} = \Sigma_{12} \, \delta^{\sigma\alpha} , \qquad\qquad (2.49)$$

where

$$G_2(\Sigma) = \left[ z \, I_2 - \Sigma_2 \right]^{-1} .$$

In Eq. (2.49), $\Sigma_2$ and $\Sigma_{12}$ are (nxn) and (mxn) matrices made out of partitioning the self-energy $\Sigma$, such that the cluster has m sites and n=N-m, N being the total number of sites. Substituting Eq. (2.49) in Eq. (2.48) one easily gets,

$$\mathfrak{x}^{\sigma\sigma'} = \Sigma_{12} \, G_2 \, \Sigma_{12}^{\dagger} \, \delta^{\sigma\sigma'} . \qquad\qquad (2.50)$$

We note that $G_2(\Sigma) = \mathscr{g}^{(\mathbb{C})}$. The subscript $\mathbb{C}$ inside the parenthesis implies that, $\mathscr{g}^{(\mathbb{C})}$ is the Green's function of the effective medium, calculated on the lattice from which the cluster $\mathbb{C}$ has been removed. Therefore, we write

$$\mathfrak{x}^{\sigma\sigma'} = \Sigma_{12} \, \mathscr{g}^{(\mathbb{C})} \, \Sigma_{12}^{\dagger} \, \delta^{\sigma\sigma'} . \qquad\qquad (2.51)$$

This completes the first step.  The rank of the matrices $H_1$ and $\hat{x}$ is $mxM^m$, where M is the number of  species  in  the alloy.

In the next step, we again partition $\Psi_1$ into a  subspace $\psi_1$ spanned by $\{|i,f\rangle, \ i \in \mathbb{C} \}$,  and  its  complement  $\psi_2$  ,  spanned by $\{|i,f_\sigma \rangle, \ \sigma \neq \emptyset, \ i \in \mathbb{C} \}$.  The  partition  theorem gives us the configuration averaged Green's function  in  the cluster subspace, i.e.

$$\left[\langle G \rangle \right]_{\mathbb{C}} = \left( z \ I \ - \ h_1 \ - \ h_{12} \ \Gamma \ h_{12}^\dagger \right)^{-1} , \tag{2.52}$$

where,

$$h_1 = \rho_1 \ \hat{H} \ \rho_1 \ ,$$

$$h_{12} = \rho_1 \ \hat{H} \ \rho_2 \ ,$$

$$\Gamma = (z \ I \ - \ h_2)^{-1} \ , \tag{2.53}$$

and

$$h_2 = \rho_2 \ \hat{H} \ \rho_2 \ .$$

Here $\rho_i$ is the projection operator in  the  subspace  $\psi_i$ and can be written as

$$\rho_1 = \ |f\rangle\langle f| \ ,$$

and,

$$\rho_2 = \sum_{\sigma \neq \emptyset} |f_\sigma \rangle\langle f_\sigma| . \tag{2.54}$$

We note that,

$$h_{12} = |f\rangle\langle f| \; \hat{H} \left[ \sum_{\sigma \neq \emptyset} |f_\sigma\rangle\langle f_\sigma| \right] = \sum_{\sigma \neq \emptyset} |f\rangle H^{\emptyset\sigma}\langle f_\sigma| . \qquad (2.55)$$

From Eqs. (2.47) and (2.51), it follows that Eq. (2.55) can be rewritten as,

$$h_{12}^{\sigma\sigma'} = H_1^{\emptyset\sigma'} \delta_{\sigma\emptyset} \; ,(\sigma' \neq \emptyset ). \qquad (2.56)$$

We know that, $H_1$ , which is defined in in the subspace $\Psi_1$ , contains the real cluster, and hence, is independent of the self-energy $\Sigma$ (Ref. 58). Thus we can write,

$$h_{12} = K . \qquad (2.57)$$

We can also write

$$h_1 = \hat{H}^{\emptyset\emptyset} = H_1^{\emptyset\emptyset} + \mathfrak{X}^{\emptyset\emptyset} . \qquad (2.58)$$

We know that $H_1$ is the random Hamiltonian in the cluster subspace. Therefore, by the augmented space theorem, $H_1^{\emptyset\emptyset}$ is the configuration averaged Hamiltonian of the cluster, which is nothing but the virtual crystal Hamiltonian, i.e.

$$H_1^{\emptyset\emptyset} = H_{vc} . \qquad (2.59)$$

Therefore, Eq. (2.52) can now be written as

$$\left[ \langle G \rangle \right]_{\mathbb{C}} = \left[ z\, I - H_{vc} - \mathscr{X} - K \prod (\Sigma) K^{\dagger} \right]^{-1}. \qquad (2.60)$$

This is the configuration averaged Green's function in the cluster subspace, which we get from the augmented space theorem. This Green's function is a (mxm) matrix, if we take an m-atom cluster. To get the CCPA equations, this Green's function should be equated with the Green's function of the effective medium described by the self-energy $\Sigma$. The effective Green's function in the cluster subspace can be obtained by the partitioning technique, and we get

$$\left[ \mathscr{G} \right]_{\mathbb{C}} = \left[ z\, I - \Sigma_1 - \Sigma_{12}\, \mathscr{G}^{(\mathbb{C})}\, \Sigma_{12}^{\dagger} \right]^{-1}$$

$$= \left[ z\, I - \Sigma_1 - \mathscr{X} \right]^{-1}. \qquad (2.61)$$

Here, $\Sigma_1$ is the self-energy in the cluster subspace, and is a (mxm) matrix. The self-consistency condition requires that,

$$\left[ \mathscr{G} \right]_{\mathbb{C}} = \left[ \langle G \rangle \right]_{\mathbb{C}}, \qquad (2.62)$$

which readily gives us the CCPA equation,[58]

$$\Sigma = H_{vc} + K \prod (\Sigma) K^{\dagger} = \mathscr{F}(\Sigma) \qquad (2.63)$$

In Eq. (2.63), we have suppressed the subscript 1 in $\Sigma$. Since $\Sigma$ is a symmetric matrix with identical diagonal elements, the number of independent equations given by Eq. (2.63), is $m(m-1)/2 + 1$. This number can be further reduced by exploiting the symmetry of the cluster.

## 2.5 ANALYTIC PROPERTIES OF THE CCPA GREEN'S FUNCTION

The physical properties of a system are intimately related to the analytic properties of the Green's function of the system.[74] A physically meaningful approximation must, therefore, ensure that the approximated Green's function preserves the analytic properties of the exact Green's function. These analytic properties, which can be derived from Eqs. (2.26) to (2.31), are collectively referred to as the herglotz properties, and are stated as:

(i) $G(z)$ is analytic on the entire complex cut-plane Im $z \neq 0$. Its spectrum is bounded, and $G(z)$ behaves as $1/z$ as $z \longrightarrow \infty$

(ii) Im $G(z) \leq 0$, for Im $z > 0$, and

(iii) $G^{\dagger}(z) = G(z^*)$.

The first two properties together guarantee a single-valued, continuous, and non-negative density of

states. The third condition is called the reality condition, because it is related to the fact that the spectrum of $H$ (i.e. the singularities of $G(z)$ ) is entirely on the real axis. It reflects the causality principle.

We have seen in section (2.4) that, it is enough to prove the herglotzicity of the self-energy $\Sigma(z)$ to ensure that the averaged Green's function $\langle G(z)\rangle$ be herglotz.

Let us now restrict z in a compact subspace $\mathcal{Z}$ of the upper half plane (Im z > 0), such that, whenever $z \in \mathcal{Z}$, the virtual crystal Hamiltonian $H_{vc}$ and $K$ (which is independent of $\Sigma$ ) are bounded, i.e. $\|H_{vc}\| \leq X$ and $\|K\| \leq Y$.

Let us first state and prove certain identities, which we will need in the subsequent discussions.

(a) If $A = B\ C\ B^{\dagger}$, then Im $A$ and Im $C$ have the same sign.

$$\text{Im } A = (A - A^{\dagger})/2i$$

$$= (1/2i)\ B(C - C^{\dagger})B^{\dagger}$$

$$= B\ (\text{Im } C)B^{\dagger}, \qquad\qquad (2.64)$$

from which the result follows.

(b) If $\text{Im } A > 0$, then $\text{Im } A^{-1} < 0$.

$$\text{Im } A^{-1} = (A^{-1} - (A^{-1})^{\dagger})/2i = \frac{1}{2i} \left[ A^{-1} (A^{\dagger} - A) (A^{-1})^{\dagger} \right]$$

$$= - A^{-1} (\text{Im } A) (A^{-1})^{\dagger} < 0. \qquad (2.65)$$

(c) If $\text{Im } A \geq x > 0$, then $\|A^{-1}\| \leq 1/x$.

$$\|A^{-1}\| = \left[ A^{-1}(A^{-1})^{\dagger} \right]^{1/2} = \left[ (A^{\dagger}A)^{-1} \right]^{1/2} = \left[ (A^{\dagger}A)^{1/2} \right]^{-1}$$

$$= \|A\|^{-1} = \left[ (\text{Re } A)^2 + x^2 \right]^{-1/2} \leq 1/x. \qquad (2.66)$$

*Theorem* 2.1

If $\text{Im } \Sigma < 0$ in $\mathscr{E}$, then $\text{Im } \mathscr{E}(\Sigma) < 0$.

*Proof*

Let us call $G_2^{\emptyset\emptyset} = \gamma$ and $\mathscr{X}^{\alpha\alpha} = \mathscr{X}$. Then $\gamma^{-1} = (z \, I - \Sigma)$. And since, $\text{Im } \Sigma < 0$ and $\text{Im } z > 0$, we have $\text{Im } \gamma^{-1} > 0$, which implies that,

$$\text{Im } \gamma < 0. \qquad (2.67)$$

Again, from Eq. (2.51) we get,

$$\text{Im } \mathscr{X} = \Sigma_{12} (\text{Im } \gamma) \Sigma_{12}^{\dagger} < 0. \qquad (2.68)$$

Therefore, $\hat{H} = H_1 + \hat{X} \Rightarrow \text{Im } \hat{H} < 0$, since $H_1$ is real. Also, we have

$$h_2^{\sigma\sigma'} = H_1^{\sigma\sigma'} + \hat{X}^{\sigma\sigma'} \delta_{\sigma\sigma'}, \quad (\sigma \neq 0)$$

and                                                                         (2.69)

$$\Gamma^{-1} = z \, I - h_2 \quad ,$$

which imply that,

$$\text{Im } h_2 = \text{Im } \hat{X} < 0$$

and                                                                         (2.70)

$$\text{Im } \Gamma < 0.$$

From Eq. (2.63) we get

$$\text{Im } \mathcal{F}(\Sigma) = \text{Im } (K \, \Gamma(\Sigma) \, K^\dagger) = K \, (\text{Im } \Gamma(\Sigma)) \, K^\dagger < 0. \quad (2.71)$$

We note that, Eq. (2.63) is solved iteratively as

$$\Sigma(i) = \mathcal{F}(\Sigma(i-1)). \quad (2.72)$$

Thus, Eq. (2.71) implies that, if $\text{Im } \Sigma(i) < 0$, then $\text{Im } \Sigma(i+1) < 0$, i.e. the sign of the imaginary part of the self-energy is preserved in each iteration.

Now let us consider the CCPA Green's function as given by Eq. (2.60). We have

$$\mathrm{Im}\ \left[\langle G \rangle\right]^{-1} = \mathrm{Im}\ (z\ I - \mathfrak{X}) - K\ (\mathrm{Im}\ \Gamma)\ K^{\dagger}. \qquad (2.73)$$

We have seen that for $\mathrm{Im}\ \Sigma < 0$, $\mathrm{Im}\ \mathfrak{X} < 0$ and $\mathrm{Im}\ \Gamma < 0$, which readily proves that, $\mathrm{Im}\ \left[\langle G \rangle\right]^{-1} > 0$, and therefore,

$$\mathrm{Im}\ \langle G \rangle < 0, \qquad (2.74)$$

in the plane $\mathrm{Im}\ z > 0$. This condition guarantees a positive density of states.[58]

*Theorem* 2.2

If $\|\Sigma\|$ is bounded, so is $\|\mathfrak{F}(\Sigma)\|$.

*Proof*    We know that $\mathrm{Im}\ (z I - \Sigma) \geq x > 0$ for $z \in \mathfrak{F}$ and $\mathrm{Im}\ \Sigma < 0$. This implies that $\|\gamma\| \leq 1/x$. Hence, from Eq. (2.51) we get,

$$\|\mathfrak{X}\| \leq \|\Sigma\|\ \|\gamma\|\ \|\Sigma\|$$

$$\leq q^2/x, \qquad (2.75)$$

where $\|\Sigma\| \leq q$. Since $H_{vc}$ is bounded above by X, we have

$$\|\hat{H}\| \leq X + \|\mathfrak{X}\| \leq X + q^2/x, \qquad (2.76)$$

and so it is also bounded above. Now from Eq. (2.63) we note that

$$\|\mathfrak{F}(\Sigma)\| \leq \|H_{vc}\| + \|K\|^2 \|\Gamma(\Sigma)\|. \tag{2.77}$$

And Im $\Gamma^{-1} \geq r > 0$ (see proof of proposition 2.1), implies that $\|\Gamma(\Sigma)\| \leq 1/r$, so that we have

$$\|\mathfrak{F}(\Sigma)\| \leq X + Y^2/r, \tag{2.78}$$

and thus is bounded. Thus, the self-energy is always bounded in the iteration procedure, if the starting value is bounded.

*Theorem* 2.3

The iterative chain $\Sigma(n+1) = \mathfrak{F}(\Sigma(n))$ converges to a unique solution, provided $-\text{Im}\ \mathfrak{X}(n) \geq x > 0$ and $-\text{Im}\ \Sigma(n) \geq Y > 0$ at each stage of the iteration and $\Sigma(0)$ and $K$ are bounded to start with. Here the indices inside the parentheses indicate the number of iteration in the chain.

*Proof*

The iteration scheme for the self-energy can be written from Eq. (2.63) as

$$\Sigma(m) = \mathfrak{F}(\Sigma(m-1)) = H_{vc} + K\ \Gamma(m-1)\ K^{\dagger}, \tag{2.79}$$

where,

$$\Gamma(m) = \left[ z \, I - H_1 - \mathfrak{X}(m) \right]^{-1}, \qquad (2.80)$$

at the m-th iteration. We can rewrite Eq. (2.52) as

$$\mathfrak{X} = \sum \mathcal{G} \, \Sigma^{\dagger}. \qquad (2.81)$$

Here we have suppressed the subspace indices in $\sum$ and $\mathcal{G}$ for convenience, and these may be restored wherever appropriate.

For the proof, we shall pick only the even steps in the iteration,[58] i.e. for m even,

$$\mathfrak{X}(m-1) = \sum(m-2) \, \mathcal{G}(m-2) \, \Sigma^{\dagger}(m-3) \qquad (2.82)$$

and,

$$\mathfrak{X}(m) = \sum(m-2) \, \mathcal{G}(m-1) \, \Sigma^{\dagger}(m-3) \qquad (2.83)$$

where,

$$\mathcal{G}(m) = \left( z \, I - \sum(m) \right)^{-1}. \qquad (2.84)$$

Thus our iteration scheme is as follows:[58]

$$\sum(0) \longrightarrow \mathfrak{X}(1) = \sum(0) \, \mathcal{G}(0) \, \Sigma^{\dagger}(-1) \longrightarrow \sum(1) \longrightarrow$$

$$\mathfrak{X}(2) = \sum(0) \, \mathcal{G}(1) \, \Sigma^{\dagger}(-1) \longrightarrow \sum(2) \longrightarrow \mathfrak{X}(3) = \sum(2) \, \mathcal{G}(2) \, \Sigma^{\dagger}(1)$$

$$\longrightarrow \sum(3) \longrightarrow \mathfrak{X}(4) = \sum(2) \, \mathcal{G}(3) \, \Sigma^{\dagger}(1) \longrightarrow \text{ and so on,}$$

where, $\Sigma(0) = \Sigma(-1)$ is our starting self-energy which we assume to be bounded and herglotz.

From Eq. (2.79) we have,

$$\Delta\Sigma(m) = \Sigma(m) - \Sigma(m-1) = K\left[\Gamma(m-1) - \Gamma(m-2)\right]K^\dagger$$

$$= K\,\Gamma(m-1)\left[\Gamma^{-1}(m-2) - \Gamma^{-1}(m-1)\right]\Gamma(m-2)K^\dagger. \qquad (2.85)$$

With the help of Eq. (2.80), it can be rewritten as

$$\Delta\Sigma(m) = K\,\Gamma(m-1)\left[\mathscr{X}(m-1) - \mathscr{X}(m-2)\right]\Gamma(m-2)K^\dagger$$

$$= K\,\Gamma(m-1)\,\Delta\mathscr{X}(m-1)\,\Gamma(m-2)K^\dagger. \qquad (2.86)$$

By a similar procedure, from Eqs. (2.82) and (2.83), we can get

$$\Delta\mathscr{X}(m) = \mathscr{X}(m) - \mathscr{X}(m-1)$$

$$= \Sigma(m-2)\,\mathscr{G}(m-1)\,\Delta\Sigma(m-1)\,\mathscr{G}(m-2)\,\Sigma^\dagger(m-3). \qquad (2.87)$$

Since, $\mathrm{Im}\left[\mathscr{G}(m)\right]^{-1} \geq Y > 0$, we can define, $\mathrm{Im}\left[\mathscr{G}(m)\right]^{-1} = (1/\alpha_m)^2$ and hence, Eq. (2.87) can be written as

$$\Delta\mathscr{X}(m) = Y^\dagger_{m-1}\,\alpha_{m-1}\,\Delta\Sigma(m-1)\,\alpha_{m-2}\,Y_{m-2} \qquad (2.88)$$

with

$$Y_m = \mathscr{G}(m)\,\Sigma^\dagger(m-1)/\alpha_m. \qquad (2.89)$$

We shall now polar decompose[75] $Y_m$ as $W_m J_m$ where $J_m = (Y_m^\dagger Y_m)^{1/2}$ and $W_m$ is a partial isometry from the range of $J_m$ to the range of $Y_m$ and thus $\|W_m\|^2 = 1$. With this we can write Eq. (2.88) as

$$\Delta \mathcal{X}(m) = J_{m-1} \left\{ W_{m-1}^\dagger \, \alpha_{m-1} \, \Delta \Sigma(m-1) \, \alpha_{m-2} \, W_{m-2} \right\} J_{m-2} \; . \qquad (2.90)$$

In a similar manner, defining $\text{Im} \left[ \Gamma(m) \right]^{-1} = (1/\beta_m)^2 \geq x > 0$, we may write Eq. (2.86) as

$$\Delta \Sigma(m) = \mathcal{J}_{m-1} \left\{ W_{m-1}^\dagger \, \beta_{m-1} \, \Delta \mathcal{X}(m-1) \, \beta_{m-2} \, W_{m-2} \right\} \mathcal{J}_{m-2}$$

$$= \mathcal{J}_{m-1} \, \mathcal{A}_{m-1} \, \mathcal{J}_{m-2} \; , \qquad (2.91)$$

where,

$$\mathcal{J}_m = (\mathcal{Y}_m^\dagger \mathcal{Y}_m)^{1/2} \quad \text{with} \quad \mathcal{Y}_m = \Gamma(m) \, K^\dagger / \beta_m$$

and,

$$\mathcal{A}_m = W_m^\dagger \, \beta_m \, \Delta \mathcal{X}(m) \, \beta_{m-1} \, W_{m-1} \; . \qquad (2.92)$$

With the help of Eqs. (2.90) and (2.91), we can write Eq. (2.92) as

$$\mathcal{A}_m = \left[ W_m^\dagger \, \beta_m \, J_{m-1} \, W_{m-1}^\dagger \, \alpha_{m-1} \, \mathcal{J}_{m-2} \right] \mathcal{A}_{m-2}$$

$$\times \left[ \mathcal{J}_{m-3} \, \alpha_{m-2} \, W_{m-2} \, J_{m-2} \, \beta_{m-1} \, W_{m-1} \right] . \qquad (2.93)$$

Now,

$$\left\| \mathcal{G}_{m-2}\ \alpha_{m-1}\ W_{m-1} \right\|^2 \le \sup_{\varphi} \langle\varphi|\ \alpha_{m-1}\ \mathcal{G}^{\dagger}_{m-2}\ \mathcal{G}_{m-2}\ \alpha_{m-1}|\varphi\rangle / \left\|\varphi\right\|^2 ,$$

$$(2.94)$$

because $\left\|W_m\right\|^2 = 1$. Here, $\sup_{\varphi} \langle\varphi|Q^{\dagger}Q|\varphi\rangle / \left\|\varphi\right\|^2$ means the maximum among all the elements $\langle\varphi|Q^{\dagger}Q|\varphi\rangle / \left\|\varphi\right\|^2$ for all states $|\varphi\rangle$ of the Hilbert space in which $Q$ is defined. In other words, it is the upper bound of the operator $Q$. We observe that,

$$\mathcal{G}^{\dagger}_{m-2}\ \mathcal{G}_{m-2} = \mathcal{Y}^{\dagger}_{m-2}\mathcal{Y}_{m-2} = K\ \Gamma^{\dagger}(m-2)\ \Gamma(m-2)\ K^{\dagger}/(\beta_{m-2})^2$$

$$= K\ \Gamma^{\dagger}(m-2)\ \left[\text{Im}\ \Gamma^{-1}(m-2)\right]\ \Gamma(m-2)\ K^{\dagger}$$

$$= K\ \Gamma^{\dagger}(m-2)\left[\frac{1}{2i}\left[\Gamma^{-1}(m-2) - \left\{\Gamma^{-1}(m-2)\right\}^{\dagger}\right]\right]\Gamma(m-2)K^{\dagger}$$

$$= K\ \left[\frac{1}{2i}\left(\Gamma^{\dagger}(m-2) - \Gamma(m-2)\right)\right]\ K^{\dagger}$$

$$= K\ \left(-\text{Im}\ \Gamma(m-2)\right)\ K^{\dagger} = = -\text{Im}\ \mathcal{J}(\Sigma(m-2))$$

$$= -\text{Im}\ \Sigma(m-1). \qquad (2.95)$$

Thus, from Eq. (2.94) we have

$$\left\|\mathcal{G}_{m-2}\ \alpha_{m-1}\ W_{m-1}\right\|^2 \le \sup_{\varphi} \langle\varphi|\ \alpha_{m-1}\ (-\text{Im}\ \Sigma(m-1))\ \alpha_{m-1}|\varphi\rangle / \left\|\varphi\right\|^2 .$$

$$(2.96)$$

We now define $|\chi\rangle = \alpha_{m-1} |\varphi\rangle$, and then Eq. (2.96) becomes

$$\|\mathscr{G}_{m-2} \; \alpha_{m-1} \; W_{m-1}\|^2 \leq \sup_{\chi} \frac{\langle \chi| \; (- \text{Im} \sum(m-1))|\chi\rangle}{\langle \chi| \; (1/\alpha_{m-1})^2 \; |\chi\rangle}$$

$$\leq \sup_{\chi} \frac{\langle \chi| \; (- \text{Im} \sum(m-1))|\chi\rangle}{\langle \chi| \; \text{Im} \; (\mathscr{G}^{-1}(m-1))|\chi\rangle} \qquad (2.97)$$

Now from Eq. (2.79) and (2.84) we observe that

$$\text{Im} \; \sum(m-1) = \text{Im} \; \mathfrak{Y}(m-2)$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.98)$

$$\mathscr{G}^{-1}(m-1) = (G_{vc})^{-1} - \mathfrak{Y}(m-1),$$

where,

$$\mathfrak{Y}(m-2) = K \; \Gamma(m-2) \; K^{\dagger}. \qquad (2.99)$$

Thus, Eq. (2.97) readily gives us

$$\|\mathscr{G}_{m-2} \; \alpha_{m-1} \; W_{m-1}\|^2 \leq$$

$$\sup_{\chi} \frac{\langle \chi| \; (- \text{Im} \; \mathfrak{Y}(m-2))|\chi\rangle}{\langle \chi| \text{Im} \; (G_{vc})^{-1}|\chi\rangle + \langle \chi| \; (-\text{Im} \; \mathfrak{Y}(m-2))|\chi\rangle}. \qquad (2.100)$$

Now, since $\text{Im} \; (G_{vc})^{-1} \geq a > 0$ and $- \text{Im} \; \mathfrak{Y} = - \text{Im} \sum \geq b > 0$, the above expression becomes

$$\left\| \mathcal{J}_{m-2} \; \alpha_{m-1} \; W_{m-1} \right\|^2 \leq b/(a+b), \text{ with a and b} > 0. \quad \text{Thus} \quad \text{we}$$

immediately get

$$\left\| \mathcal{J}_{m-2} \; \alpha_{m-1} \; W_{m-1} \right\|^2 = \lambda_1 < 1. \qquad (2.101)$$

In an exactly similar manner, we can get

$$\left\| J_{m-1} \; \beta_m \; W_m \right\|^2 = \lambda_2 < 1. \qquad (2.102)$$

Thus, from Eq. (2.93) we have

$$\left\| \mathcal{A}_m \right\| \leq \lambda^2 \; \left\| \mathcal{A}_{m-2} \right\|, \text{ where } \lambda = (\lambda_1 \lambda_2)^{1/2} < 1$$

$$\rightarrow \left\| \mathcal{A}_m \right\| \leq \lambda^m \; \left\| \mathcal{A}_0 \right\|. \qquad (2.103)$$

From Eq. (2.91) we get

$$\left\| \Delta\textstyle\sum(m) \right\| \leq \left\| \mathcal{J}_{m-1} \right\| \; \left\| \mathcal{J}_{m-2} \right\| \; \left\| \mathcal{A}_{m-2} \right\|. \qquad (2.104)$$

Since, $\mathcal{J}_m^\dagger \mathcal{J}_m = - \text{Im} \sum(m+1)$ (from Eq. (2.95)), and $\sum(m+1)$ is always bounded, if we start from a bounded $\sum(0)$ ( see proposition 2.2), we have $\left\| \mathcal{J}_m \right\| \leq \eta$, where $\eta$ is some finite number. The same is true for an initial bounded starting $\left\| \mathcal{A}_0 \right\|$. Thus from Eqs. (2.103) and (2.104), we finally get,

$$\left\| \Delta \Sigma (m) \right\| \leq \eta^2 \lambda^{m-1} \left\| \mathscr{A}_0 \right\|. \qquad (2.105)$$

which implies that

$$\left\| \Sigma(p) - \Sigma(q) \right\| \leq \eta^2 \left\| \mathscr{A}_0 \right\| \sum_{j=q}^{p-1} \lambda^j \longrightarrow 0 \text{ as } p, q \longrightarrow \infty.$$

Thus $\Sigma(m)$'s form a Cauchy sequence and, therefore, will converge to a unique value as $m \longrightarrow \infty$.[58] This condition is sometimes called the Fixed point theorem. Note that, the only assumption, we made was that, the starting value for $\Sigma$ is bounded and herglotz. In practice, one usually starts off with the CPA value, which conforms to the above assumptions. Thus, our proof is complete.

## 2.6 CONCLUSION

In this chapter, we presented the augmented space formalism, and derived the CCPA self-consistent equations using this formulation. This CCPA restores the translational symmetry of the effective medium. We also showed that, our CCPA gives an approximated averaged Green's function, which retains the analytic properties of the exact Green's function and that, the self-consistent iteration scheme for the self-energy has a fixed point, i.e. it converges to a unique,

bounded, and herglotz self-energy if we start off with a bounded and herglotz one. This guarantees a non-negative density of states, which is a single-valued function of the energy.

The augmented space formalism presented in this chapter can not deal with the systems with short-range order. In Chapter 5, we will tackle the problem of incorporating the short-range order in this formalism.

# CHAPTER 3
# THE KORRINGA-KOHN-ROSTOKER
# CLUSTER COHERENT-POTENTIAL APPROXIMATION

## 3.1 INTRODUCTION

The Korringa-Kohn-Rostoker (KKR) coherent-potential approximation[6-8,12] (CPA) provides a reliable and realistic description of band structure and related electronic properties of disordered alloys.[76-83] In this method, the one-electron alloy potential is constructed of muffin-tin potentials, which are non-overlapping spherically symmetric potentials centered on the sites of the lattice. In the beginning, Lloyd's formula[84] was used in all the electronic structure calculations for alloys described by a muffin-tin Hamiltonian. The Lloyd's formula gives an expression for the density of states for a system that is made up of an array of muffin-tin potentials. This expression was manipulated to derive the expression for the averaged density of states for alloys. However, the component and l-decomposed density of states, and Bloch spectral density function, when calculated using the Lloyd's formula become negative in some energy regions.[12,66] Moreover, one can not calculate charge densities in the scheme of Lloyd's formula. The component

charge densities are essential for a fully charge self-consistent[8,12] implementation of the KKR-CPA within the local density approximation of the density functional theory.[13-15]

This realization led to the development of Green's function formalism[12] for disordered alloys. In this formalism, one calculates the configuration averaged Green's function, from which various electronic properties of the alloy can be calculated. Within this formalism, one can calculate the charge densities, and therefore, it can be made fully charge self-consistent, within the local density approximation of the density functional theory. For this reason, the KKR-CPA is rightly called a first-principles parameter-free theory of substitutionally disordered alloys. Due to the development of fast $k$-space integration schemes,[85,86] it has been possible to use KKR-CPA to calculate the electronic properties of a wide range of disordered alloys. Now the KKR-CPA has reached the same level of sophistication as the KKR band theory of pure metals.[8] A relativistic version of the KKR-CPA has also been reported.[87]

In spite of all the successes it achieved, the KKR-CPA remains a single-site approximation. In the KKR-CPA, the real disordered medium is replaced by a translationally symmetric effective medium with an effective scatterer on

each site of the lattice. The effective medium is determined by a self-consistency condition that, the average extra scattering, with respect to the medium, from a single real atom embedded in the effective medium be zero. The KKR-CPA might fail whenever a single-site effective medium description becomes inadequate, e.g. in presence of strong local environmental effects, such as short range order and clustering tendencies. These local environmental effects can be investigated, accurately and convincingly, only through a cluster or multisite approximation.

In Chapter 2, we presented the augmented space formalism[52-55] and a self-consistent cluster coherent-potential approximation[46,58] (CCPA) in which one can go beyond the CPA in a systematic way. In this method the effective medium is determined by a self-consistency condition that, average extra scattering, with respect to the medium, from cluster of real atoms embedded in the effective medium be zero. We also noted that, the CCPA restores the translational symmetry of the effective medium. The ideas of the augmented space formalism are rather general and can be incorporated within the conventional KKR method as well. We have successfully combined these two methods and have developed a self-consistent CCPA in the KKR framework,[67] which we call KKR-CCPA. Within this formulation, one can calculate the charge densities, and therefore, can achieve

charge self-consistency within the local density approximation of the density functional theory. Therefore, our KKR-CCPA formulation is a first-principles parameter-free theory of disordered alloys, in which correlated scattering from two or more sites are taken into account. The extension of this theory to ternary alloys is straightforward.[68]

The outline of this chapter is as follows. In section 3.2 we give a brief review of the KKR Green's function formalism. Various equations in this section are presented in a form that lend themselves quite naturally to the cluster generalization. In section 3.3, we present the KKR-CCPA formulation. Although, there is no site-off-diagonal disorder in the KKR framework, the KKR-CCPA, quite predictably, introduces site-off-diagonal corrections as well in the scattering matrices along with the usual site-diagonal corrections.[67] In section 3.4, we derive the expression for the configuration averaged Green's function[88] within the KKR-CCPA, from which averaged electronic properties of an alloy can be calculated. In section 3.5, the problem of embedding a cluster of real impurities in the effective medium and the determination of local properties, are discussed. Finally in section 3.6, we give our conclusions about the implementation of the KKR-CCPA.

## 3.2 THE KKR GREEN'S FUNCTION FORMALISM

Consider a disordered substitutional alloy $A_x B_y$ . The one-electron Hamiltonian for a certain configuration of the alloy can be written (in atomic units) as,

$$H = - \nabla^2 + \sum_i v_i(\vec{r} - \vec{R}_i) = - \nabla^2 + \sum_i v_i(\vec{r}_i), \qquad (3.1)$$

where $R_i$'s are the site locations and $v_i(\vec{r}_i)$ are the potentials centered at $\vec{R}_i$ . The potentials $v_i(\vec{r}_i)$ are random, and can be $v_A(\vec{r}_i)$ or $v_B(\vec{r}_i)$ depending upon the occupancy of the i-th site. We assume that $v_i(\vec{r}_i)$ are of muffin-tin type and do not overlap with each other:

$$v_i(\vec{r}_i) = v_i(r_i) \, \Theta(r_M - r_i) \qquad (3.2)$$

where $r_M$ is the muffin-tin radius, and $\Theta(x)$ is the step function, which is 1 when $x \geq 0$, and vanishes for $x < 0$.

The Green's function for this system can be written in operator notation as,[12]

$$G = G_o + G_o \, T \, G_o , \qquad (3.3)$$

where $G_o$ is the free electron Green's function, and $T$ is the total scattering operator of the system, and is given by Dyson equation:

$$T = V + V G_o T , \qquad (3.4)$$

where $V$ is the total crystal potential. The operator $T$ may be written as

$$T = \sum_{ij} T^{ij} \qquad (3.5)$$

where $T^{ij}$ are called scattering-path-operators,[8,12] and are defined as

$$T^{ij} = t^i \delta_{ij} + t^i G_o \sum_{k \neq i} T^{kj}. \qquad (3.6)$$

Here

$$t^i = v_i ( I + G_o t^i ), \qquad (3.7)$$

is the t-matrix that describes the scattering from the potential on the i-th site. Due to the spherical symmetry of the potentials, the single-site t-matrices are diagonal in the angular momentum space, and their on-the-energy-shell matrix elements are given by[6,8]

$$t^i_{LL'} = -(\varkappa)^{-1} \exp[\,i\delta^{(i)}_l\,]\ \sin\delta^{(i)}_l\ \delta_{LL'} = t^i_l\ \delta_{LL'} \qquad (3.8)$$

where $L \equiv (l,m)$ is a composite index, $\varkappa = E^{1/2}$ and $\delta^{(i)}_l$ are the phase-shifts for the potential $v_i(r_i)$.

The free electron Green's function, when projected onto the real space takes the form[6,8]

$$G_o(\vec{r}, \vec{r}\,') = -i\varkappa \sum_L Y_L(\hat{r})\ j_l(\varkappa r_<)\ h_l(\varkappa r_>)\ Y_L(\hat{r}\,') \qquad (3.9)$$

where $r_<(r_>)$ is the smaller (greater) of the variables $r$ and $r'$, $Y_L(\hat{r})$ is a real spherical harmonic, and $j_l(x)$ and $h_l(x)$ are the spherical Bessel and outgoing Hankel functions respectively.

We will derive the expression for $G(\vec{r},\vec{r}\,')$ from Eq. (3.3) for two different cases; the site-diagonal case, when both $\vec{r}$ and $\vec{r}\,'$ are inside some i-th cell, and the non-site-diagonal case, when $\vec{r}$ and $\vec{r}\,'$ are in different cells.[12] Taking the projection of Eq. (3.3) onto the real space, for these two different cases, we get

$$G(\vec{r},\vec{r}\,') = \sum_{LL'} Z^i_L(\vec{r}_i)\ T^{ij}_{LL'}\ Z^j_{L'}(\vec{r}\,'_j) - \delta_{ij} \sum_L Z^i_L(\vec{r}_i)\ J^i_L(\vec{r}\,'_j),$$

$$(3.10)$$

where $\vec{r}_i$ and $\vec{r}'_j$ lie on i-th and j-th cells respectively. The functions $Z_L^i(\vec{r}_i)$ and $J_L^i(\vec{r}_i)$ are respectively the regular and irregular solutions of the Schrödinger equation for a single muffin-tin potential,[12] i.e.

$$[- \nabla^2 + v_i(\vec{r}_i) - E ] \begin{cases} Z_L^i(\vec{r}_i) \\ J_L^i(\vec{r}_i) \end{cases} = 0, \qquad (3.11)$$

and are normalized such that at $r_i = r_M$ , they join smoothly to

$$Z_L^i(\vec{r}_i) = Y_L(\hat{r}_i) \left[ j_l(\varkappa r_i) C_l^i - i \varkappa h_l(\varkappa r_i) \right] \qquad (3.12)$$

and

$$J_L^i(\vec{r}_i) = Y_L(\hat{r}_i) j_l(\varkappa r_i) \qquad (3.13)$$

where

$$C_l^i = (t_l^i)^{-1} = - \varkappa \cot\delta_l^{(i)} + i\varkappa. \qquad (3.14)$$

In Eq. (3.10), $T_{LL'}^{ij}$ are on-the-energy-shell matrix elements of scattering-path operators. These can be obtained from Eq. (3.6) by simple algebraic manipulation to give,[12]

$$T_{LL'}^{ij} = ( A^{-1})_{LL'}^{ij} , \qquad (3.15)$$

where,

$$A_{LL'}^{ij} = C_l^i \delta_{LL'} \delta_{ij} - B_{LL'}^{ij} . \qquad (3.16)$$

$B_{LL'}^{i,j}$ are the real space version of the well-known KKR structure constants,[6,8] and are given by

$$B_{LL'}^{i,j} = -4\pi i \varkappa \sum_{L''} i^{l-l'-l''} \Lambda_{LL'}^{L''} h_{l''}(\varkappa R_{ij}) Y_{L''}(\hat{R}_{ij}) (1-\delta_{ij})$$

$$(3.17)$$

where $\vec{R}_{ij} = \vec{R}_j - \vec{R}_i$ and $\Lambda_{LL'}^{L''}$ are Gaunt factors, given by

$$\Lambda_{LL'}^{L''} = \int Y_{L''}(\hat{x}) Y_L(\hat{x}) Y_{L'}(\hat{x}) \, d\Omega_x \ . \qquad (3.18)$$

The Fourier transform of Eq. (3.17),

$$B_{LL'}(\vec{k}) = \frac{1}{N} \sum_{i \neq j} B_{LL'}^{ij} \exp[i\vec{k}\cdot\vec{R}_{ij}] \ , \qquad (3.19)$$

are related to the KKR structure functions, $S_{LL'}(\vec{k})$ as,

$$B_{LL'}(\vec{k}) = S_{LL'}(\vec{k}) + i\varkappa \, \delta_{LL'} \ . \qquad (3.20)$$

Eqs. (3.15) and (3.16) will play a central role in our formulation. We observe that, the randomness in $T_{LL'}^{ij}$ comes from $C_l^i$'s only, while $B_{LL'}^{ij}$ depend completely on the lattice structure. Therefore, in the KKR framework, unlike as in case of tight-binding formalism, there is no off-diagonal disorder.

## 3.3 THE KKR CLUSTER CPA FORMULATION

We now apply the augmented space formalism to the KKR Green's function formalism presented in the preceding section. We will determine the configuration averaged path-operators using this formalism. The first step in this direction is to express the randomness in $A_{LL}^{ij}$, in terms of some random variables. From Eq. (3.16), the matrix $A$ can be written in an operator notation as, [67]

$$A = \sum_i c^i |i\rangle\langle i| - \sum_{ij(i \neq j)} B^{ij} |i\rangle\langle j|. \qquad (3.21)$$

In Eq. (3.21) we have suppressed the angular momentum indices. We now describe the randomness in $A$ by writing $c^i$ in terms of the random variable $n_i$ defined in Eq. (2.32), as

$$c^i = c^B + \delta c \, n_i \, , \qquad (3.22)$$

where,

$$\delta c = c^A - c^B. \qquad (3.23)$$

Substituting Eq. (3.22) in Eq. (3.21) we get

$$A = c^B \sum_i |i\rangle\langle i| + \delta C \sum_i |i\rangle\langle i| \, n_i - \sum_{ij(i \neq j)} B^{ij} |i\rangle\langle j|$$

$$\equiv A(\{n_i\}). \tag{3.24}$$

Our aim is to find configuration averaged $T^{ij}$, and by the augmented space theorem, Eq. (2.19) it is given by,

$$\langle T^{ij} \rangle = \langle i,f| \left[ \tilde{A}(\{M^i\}) \right]^{-1} |j,f \rangle, \tag{3.25}$$

where,

$$\tilde{A}(\{M^i\}) = \left[ c^B \sum_i |i\rangle\langle i| - \sum_{ij(i \neq j)} B^{ij} |i\rangle\langle j| \right] \otimes \sum_{f_\sigma \in \mathfrak{C}} |f_\sigma\rangle\langle f_\sigma| +$$

$$\delta C \sum_i |i\rangle\langle i| \otimes M^i. \tag{3.26}$$

The operator $M^i$ and the vectors $|f_\sigma\rangle$ are described in Chapter 2 (section 2.2). In Eq. (3.26), $\tilde{A}(\{M^i\})$ is an operator functional in the augmented space $\Psi$, and $\mathfrak{C}$ is the set of all possible vectors in the configuration space. Now, we partition the augmented space $\Psi$ into subspaces $\Psi_1$ and $\Psi_2$ in the scheme described in section 2.2 of Chapter 2. Subspace $\Psi_1$ is spanned by $\{|i;f_\sigma\rangle, i \in \mathbb{C}, f_\sigma \in \mathfrak{C}\}$, where $\mathbb{C}$ is

the chosen cluster. Subspace $\Psi_2$ is the complement of $\Psi_1$ in $\Psi$. If the cluster $\mathbb{C}$ contains m sites, then the rank of $\Psi_1$ is $m \times 2^m$. The crucial mean-field approximation now involves replacing the conjugate space $\Psi_2$ by an effective medium.

Since we need the $\langle i,f | \ldots | j,f \rangle$ element (i, $j \in \mathbb{C}$), of $\left[ \tilde{A}(\{M^i\}) \right]^{-1}$ in Eq. (3.25), we partition $\tilde{A}(\{M^i\})$ as follows,

$$\tilde{A} = \begin{bmatrix} A_1 & \vdots & A_{12} \\ \cdots & \cdots & \cdots \\ A_{21} & \vdots & A_2 \end{bmatrix}, \tag{3.27}$$

where $A_1$ is in the subspace $\Psi_1$ and $A_2$ is in the subspace $\Psi_2$. By applying partition theorem, the inverse of $\tilde{A}$ in subspace $\Psi_1$ can be written as,

$$[\tilde{A}^{-1}]_1 = \left[ A_1 - A_{12} A_2^{-1} A_{21} \right]^{-1} = \hat{A}^{-1}. \tag{3.28}$$

The four constituent matrices of $\tilde{A}$ are given by,

$$A_1 = c^B \sum_{i \in \mathbb{C}} |i\rangle\langle i| \otimes \sum_{f_\alpha \in \mathbb{C}'} |f_\alpha\rangle\langle f_\alpha| + \delta c \sum_{i \in \mathbb{C}} |i\rangle\langle i| \otimes M^i$$

$$- \sum_{\substack{ij \in \mathbb{C} \\ (i \neq j)}} B^{ij} |i\rangle\langle j| \otimes \sum_{f_\alpha \in \mathbb{C}'} |f_\alpha\rangle\langle f_\alpha|, \tag{3.29}$$

$$A_2 = \left[ C_{eff} \sum_{k \in \mathbb{C}'} |k\rangle\langle k| - \sum_{\substack{kl \in \mathbb{C}' \\ (k \neq l)}} b^{kl} |k\rangle\langle l| - \right.$$

$$\left. \sum_{\substack{kl \in \mathbb{C}' \\ (k \neq l)}} B^{kl} |k\rangle\langle l| \right] \otimes \sum_{f_{\sigma'} \in \mathbb{C}} |f_{\sigma'}\rangle\langle f_{\sigma'}| , \qquad (3.30)$$

$$A_{12} = -\left[ \sum_{i \in \mathbb{C}} \sum_{k \in \mathbb{C}'} b^{ik} |i\rangle\langle k| + \sum_{i \in \mathbb{C}} \sum_{k \in \mathbb{C}'} B^{ik} |i\rangle\langle k| \right] \otimes \sum_{f_{\sigma'} \in \mathbb{C}} |f_{\sigma'}\rangle\langle f_{\sigma'}| ,$$

$$(3.31)$$

and

$$A_{21} = A_{12}^{\dagger} .$$

In Eqs. (3.30) and (3.31), $b^{kl}$ are the site-off-diagonal corrections in $C$, the diagonal corrections already contained in $C_{eff}$. Note that, $A_1$ does not contain $b^{ij}$, because subspace $\Psi_1$ contains the real atoms and their configurations. $A_2$ has got these off-diagonal corrections, because subspace $\Psi_2$ contains only the effective atoms. This partitioning of the augmented space into subspaces $\Psi_1$ and $\Psi_2$, is different from the physical partition of the lattice into non-overlapping clusters of Tsukada scheme.[28] In the present scheme, the subspaces $\Psi_1$ and $\Psi_2$ are interacting, and therefore, the operator $A_{12}$, which connects the subspaces $\Psi_1$ and $\Psi_2$, must contain the off-diagonal corrections $b^{ik}$, in order to include correlated scattering between a site inside

the cluster and a site outside the cluster.[67] Also, this ensures that, the CCPA restores the translational invariance of the effective medium. Removing $b^{ik}$ from $A_{12}$ in Eq. (3.31) will lead to the old Tsukada scheme, which is not the same as our CCPA. In general, $b^{kl}$ will not be zero in KKR-CCPA. However, for a one-atom cluster, these terms vanish, thus reducing to the correct KKR-CPA limit.[67] For convenience, we add $b^{kl}$ to $B^{kl}$ (which are also off-diagonal in site indices) and define $B_{eff}^{kl}$ as,

$$B_{eff}^{kl} = B^{kl} + b^{kl}. \qquad (3.32)$$

Thus Eqs. (3.30) and (3.31) can now be written as,

$$A_2 = \left[ C_{eff} \sum_{k \in \mathbb{C}'} |k\rangle\langle k| - \sum_{\substack{kl \in \mathbb{C}' \\ (k \neq l)}} B_{eff}^{kl} |k\rangle\langle l| \right] \otimes \sum_{f_{\sigma} \in \mathbb{G}} |f_{\sigma}\rangle\langle f_{\sigma}| \qquad (3.33)$$

and

$$A_{12} = - \left[ \sum_{i \in \mathbb{C}} \sum_{k \in \mathbb{C}'} B_{eff}^{ik} |i\rangle\langle k| \right] \otimes \sum_{f_{\sigma} \in \mathbb{G}} |f_{\sigma}\rangle\langle f_{\sigma}|. \qquad (3.34)$$

The elements of $\hat{A}$ in Eq. (3.28), can be found if we can evaluate the triple product $(A_{12} A_2^{-1} A_{21})$. Since $A_2$ is the matrix in the effective medium with the cluster $\mathbb{C}$ removed from the lattice, we have

$$A_2^{-1} = T_{eff}^{(\mathbb{C})}. \qquad (3.35)$$

The superscript $\mathbb{C}$ inside the parenthesis indicates that $T_{eff}^{(\mathbb{C})}$ is the path operator matrix of the effective medium with the cluster removed from the lattice. It is not possible to calculate this quantity, but we will show that it can be completely eliminated from the computational procedure.[67] From Eqs. (3.33), (3.34) and (3.35) we get,

$$A_{12}\, A_2^{-1}\, A_{21} = \sum_{ij\in\mathbb{C}} \sum_{kl\in\mathbb{C}'} B_{eff}^{ik}\, T_{eff}^{(\mathbb{C})kl}\, B_{eff}^{lj}\, |i\rangle\langle j| \otimes \sum_{f_\sigma\in\mathbb{C}} |f_\sigma\rangle\langle f_\sigma|$$

$$= \sum_{ij\in\mathbb{C}} \mathfrak{X}_{\mathbb{C}}^{ij}\, |i\rangle\langle j| \otimes \sum_{f_\sigma\in\mathbb{C}} |f_\sigma\rangle\langle f_\sigma| , \qquad (3.36)$$

where,

$$\mathfrak{X}_{\mathbb{C}}^{ij} = \sum_{kl\in\mathbb{C}'} B_{eff}^{ik}\, T_{eff}^{(\mathbb{C})kl}\, B_{eff}^{lj} , \quad \text{for } i,j \in \mathbb{C}. \qquad (3.37)$$

It is clear from Eq. (3.36) that the matrix $[A_{12}\, A_2^{-1} A_{21}]$ is diagonal in the configuration space $\Phi$ . The off-diagonal parts in $\hat{A}$ thus come from $A_1$ only. From Eqs. (3.28), (3.29) and (3.37) we get,

$$\hat{A} = \left[ \sum_{i\in\mathbb{C}} (\mathbb{C}^B - \mathfrak{X}_{\mathbb{C}}^{ii})\, |i\rangle\langle i| - \sum_{\substack{ij\in\mathbb{C}\\(i\neq j)}} (B^{ij} + \mathfrak{X}_{\mathbb{C}}^{ij})\, |i\rangle\langle j| \right]$$

$$\otimes \sum_{f_\sigma\in\mathbb{C}} |f_\sigma\rangle\langle f_\sigma| + \delta\mathbb{C} \sum_{i\in\mathbb{C}} |i\rangle\langle i| \otimes M^i. \qquad (3.38)$$

Now we start the second step of the CCPA, in which $\Psi_1$ is partitioned into subspaces $\psi_1$ and $\psi_2$ such that $\psi_1$ is spanned by $\{|i;f\rangle, \ i \in \mathbb{C}\}$, and its complement $\psi_2$ is spanned by $\{|i;f_\sigma\rangle, \ \sigma \neq \emptyset, \ i \in \mathbb{C}\}$. In this scheme, we partition $\hat{A}$ as,

$$\hat{A} = \begin{pmatrix} \mathscr{A}_1 & \vdots & \mathscr{A}_{12} \\ \cdots & \vdots & \cdots \\ \mathscr{A}_{21} & \vdots & \mathscr{A}_2 \end{pmatrix}, \tag{3.39}$$

where, $\mathscr{A}_1$ is in the subspace $\psi_1$ and $\mathscr{A}_2$ is in subspace $\psi_2$. The ranks of $\mathscr{A}_1$ and $\mathscr{A}_2$ are m and $mx(2^m-1)$ respectively. The four constituent matrices of $\hat{A}$ can be written as

$$\mathscr{A}_1 = |f\rangle\langle f| \ \hat{A} \ |f\rangle\langle f|, \tag{3.40}$$

$$\mathscr{A}_{12} = |f\rangle\langle f| \ \hat{A} \left( \sum_{f_\sigma \ (\sigma \neq \emptyset)} |f_\sigma\rangle\langle f_\sigma| \right), \tag{3.41}$$

$$\mathscr{A}_2 = \left[ \sum_{f_\sigma \ (\sigma \neq \emptyset)} |f_\sigma\rangle\langle f_\sigma| \right] \hat{A} \left( \sum_{f_{\sigma'} \ (\sigma' \neq \emptyset)} |f_{\sigma'}\rangle\langle f_{\sigma'}| \right), \tag{3.42}$$

$$\mathscr{A}_{21} = \mathscr{A}_{12}^\dagger . \tag{3.43}$$

These matrices can be written explicitly with the help of following identities in the augmented space:

$$M^i \ |f\rangle = x \ |f\rangle + (xy)^{1/2} \ |f_i\rangle, \tag{3.44a}$$

$$M^1 \left| f_i \right> = y \left| f_i \right> + (xy)^{1/2} \left| f \right>, \tag{3.44b}$$

$$M^i \left| f_j \right> = x \left| f_j \right> + (xy)^{1/2} \left| f_{ij} \right>, \quad (i \neq j) \tag{3.44c}$$

$$M^i \left| f_{ij} \right> = y \left| f_{ij} \right> + (xy)^{1/2} \left| f_j \right>, \tag{3.44d}$$

$$M^i \left| f_{kj} \right> = x \left| f_{kj} \right> + (xy)^{1/2} \left| f_{ijk} \right>, \quad (kj \neq i), \tag{3.44e}$$

and so on.

The above identities can be written in a general form as,

$$M^i \left| f_\sigma \right> = x \left| f_\sigma \right> + (xy)^{1/2} \left| f_{\sigma'} \right>, \quad \sigma' = \sigma + i, \text{ when } i \notin \sigma$$

and
$$\tag{3.45}$$

$$M^i \left| f_\sigma \right> = y \left| f_\sigma \right> + (xy)^{1/2} \left| f_{\sigma'} \right>, \quad \sigma' = \sigma - i, \text{ when } i \in \sigma.$$

Therefore, we can write

$$\left< f \right| M^i \left| f_\sigma \right> = x \, \delta_{\emptyset\sigma} + (xy)^{1/2} \, \delta_{i\sigma} . \tag{3.46}$$

With the help of Eq. (3.46), we can write Eqs. (3.40) to (3.43) as

$$\mathscr{A}_1 = \sum_{i \in \mathbb{C}} (\bar{C} - \mathfrak{X}_{\mathbb{C}}^{ii}) \left| i;f \right> \left< i;f \right| - \sum_{\substack{ij \in \mathbb{C} \\ (i \neq j)}} (B^{ij} + \mathfrak{X}_{\mathbb{C}}^{ij}) \left| i;f \right> \left< j;f \right|,$$

$$\tag{3.47}$$

$$\mathscr{A}_{12} = \omega \sum_{i \in \mathbb{C}} |i;f\rangle\langle 1;f_i|, \tag{3.48}$$

$$\mathscr{A}_{21} = \omega \sum_{i \in \mathbb{C}} |i;f_i\rangle\langle i;f|, \tag{3.49}$$

and

$$\mathscr{A}_2 = \left[ \sum_{i \in \mathbb{C}} (C^B - \mathscr{X}_\mathbb{C}^{ii}) |i\rangle\langle i| - \sum_{\substack{ij \in \mathbb{C} \\ (i \neq j}} (B^{ij} + \mathscr{X}_\mathbb{C}^{ij}) |i\rangle\langle j| \right] \otimes$$

$$\sum_{\sigma \neq \emptyset} |f_\sigma\rangle\langle f_\sigma| + \delta C \sum_{i \in \mathbb{C}} |i\rangle\langle i| \otimes \sum_{\sigma \neq \emptyset} \sum_{\sigma' \neq \emptyset} |f_\sigma\rangle\langle f_\sigma| M^i |f_{\sigma'}\rangle\langle f_{\sigma'}| \tag{3.50}$$

where,

$$\overline{C} = x\,C^A + y\,C^B, \tag{3.51}$$

and

$$\omega = (xy)^{1/2}\,\delta C. \tag{3.52}$$

Now, inverse of $\hat{A}$ in subspace $\psi_1$ is given by

$$[\hat{A}^{-1}]_1 = \left[ \mathscr{A}_1 - \mathscr{A}_{12}\,\mathscr{A}_2^{-1}\,\mathscr{A}_{21} \right]^{-1}. \tag{3.53}$$

Since the ranks of the matrices $\mathscr{A}_1$, $\mathscr{A}_{12}$, $\mathscr{A}_{21}$ and $\mathscr{A}_2$ are small, it is not difficult to find the matrix elements of $[\hat{A}^{-1}]_1$ in Eq. (3.53). From Eqs. (3.48), (3.49), and (3.50) we can write

$$\mathscr{A}_{12}\ \mathscr{A}_2^{-1}\ \mathscr{A}_{21} = \omega \sum_{1j\in\mathbb{C}} |1;f\rangle\langle 1;f_i|\ \mathscr{A}_2^{-1}\ |j;f_j\rangle\langle j;f|\ \omega$$

$$= \omega\ \Gamma\ \omega, \qquad (3.54)$$

where

$$\Gamma = \sum_{1j\in\mathbb{C}} |i;f\rangle\langle i;f_i|\ \mathscr{A}_2^{-1}\ |j;f_j\rangle\langle j;f|. \qquad (3.55)$$

From Eq. (3.53) we get

$$\langle i;f|\ \hat{A}^{-1}|j;f\rangle = \langle i;f|\ (\mathscr{A}_1 - \omega\ \Gamma\ \omega\ )^{-1}|j;f\rangle. \qquad (3.56)$$

But, from Eq. (3.25), the left-hand side of Eq. (3.56) is the configuration averaged path-operator, i.e.

$$\langle T^{ij}\rangle = \langle i;f|\ (\mathscr{A}_1 - \omega\ \Gamma\ \omega\ )^{-1}|j;f\rangle. \qquad (3.57)$$

We note that, both $\mathscr{A}_1$ and $\Gamma$ are diagonal in $|f\rangle$, so that we can write

$$\langle T^{ij}\rangle = \langle i|\ (A_1 - \omega\ Q\ \omega\ )^{-1}|j\rangle, \qquad (3.58)$$

where

$$A_1 = \langle f|\ \mathscr{A}_1\ |f\rangle$$

$$= \sum_{i\in\mathbb{C}}(\bar{C} - \mathfrak{x}_{\mathbb{C}}^{ii})\ |i\rangle\langle i| - \sum_{\substack{ij\in\mathbb{C}\\(i\neq j)}}(B^{ij}+\mathfrak{x}_{\mathbb{C}}^{ij})\ |i\rangle\langle j| \qquad (3.59)$$

and

$$Q = \langle f| \; \boxed{\phantom{x}} \; |f\rangle = \sum_{ij \in \mathbb{C}} |i\rangle\langle i;f_i| \; \mathscr{A}_2^{-1} \; |j;f_j\rangle\langle j|. \qquad (3.60)$$

Now consider a translationally invariant effective medium for which the path-operators are given as

$$T_{eff}^{ij} = \left[ A_{eff}^{-1} \right]^{ij}, \qquad (3.61)$$

where

$$A_{eff} = C_{eff} \sum_i |i\rangle\langle i| - \sum_{\substack{ij \\ (i \neq j)}} B_{eff}^{ij} |i\rangle\langle j|. \qquad (3.62)$$

We need the path-operators of the effective medium in the cluster subspace, which we get by partitioning technique, i.e.

$$T_{eff}^{ij} = \langle i| \left[ \sum_{k \in \mathbb{C}} (C_{eff} - \tilde{x}_{\mathbb{C}}^{kk}) |k\rangle\langle k| - \right.$$

$$\left. \sum_{\substack{kl \in \mathbb{C} \\ (k \neq l)}} (B_{eff}^{kl} + \tilde{x}_{\mathbb{C}}^{kl}) |k\rangle\langle l| \right]^{-1} |j\rangle. \qquad (3.63)$$

The self-consistency condition requires that the averaged path-operators obtained by the augmented space formalism should be equal to the path-operators of the effective medium, i.e.

$$\langle T^{ij} \rangle = T_{eff}^{ij} \quad , \tag{3.64}$$

which implies that ,

$$A_1 - \omega \, Q \, \omega = \sum_{i \in \mathbb{C}} (C_{eff} - \mathcal{X}_{\mathbb{C}}^{ii}) \, |i\rangle\langle i|$$

$$- \sum_{\substack{ij \in \mathbb{C} \\ (i \neq j)}} (B_{eff}^{ij} + \mathcal{X}_{\mathbb{C}}^{ij}) \, |i\rangle\langle j| . \tag{3.65}$$

The KKR-CCPA equations follow directly from Eq. (3.65), if we compare the corresponding matrix elements on both sides,

$$C_{eff} = \bar{C} - \omega \, \langle i;f_i| \, \mathscr{A}_2^{-1} |i;f_i\rangle \, \omega, \tag{3.66}$$

$$b^{ij} = \omega \, \langle i;f_i| \, \mathscr{A}_2^{-1} |j;f_j\rangle \, \omega, \text{ for } ij(i \neq j) \in \mathbb{C} \quad . \tag{3.67}$$

We note that, Eqs. (3.66) and (3.67) are self-consistent equations, which involve $C_{eff}$ , $b^{ij}$, and $\mathcal{X}_{\mathbb{C}}^{ij}$ on the right-hand side as well. These equations can be solved iteratively; the starting values for $C_{eff}$ and $b^{ij}$ may be taken as $\bar{C}$ and 0 respectively. From Eq. (3.63), it is evident that, $\mathcal{X}_{\mathbb{C}}^{ij}$ can be expressed in terms of $\{T_{eff}^{ij}\}$, $\{B_{eff}^{ij}\}$ (i, j $\in \mathbb{C}$), and $C_{eff}$ , i.e.

$$x_{\mathbb{C}}^{ij} \equiv x_{\mathbb{C}}^{ij} \left[ \{T_{eff}^{ij}\},\ C_{eff}\ ,\ \{B_{eff}^{ij}\},\ i,\ j \in \mathbb{C} \right]. \qquad (3.68)$$

In Chapter 4, we will show that, for a two-atom cluster, Eq. (3.68) can be cast into a very simple expression. The path-operators appearing in Eq. (3.68) can be calculated by the usual $\vec{k}$-space integration over the first Brillouin zone,

$$T_{eff}^{ij} = \frac{\Omega}{8\pi^3} \int_{BZ} [\ C_{eff} - B_{eff}(\vec{k})\ ]^{-1} \exp[\ -i\vec{k}.\vec{R}_{ij}\ ]\ d\vec{k} \qquad (3.69)$$

where $B_{eff}(\vec{k})$ is the Fourier transform of $B_{eff}^{ij}$ i.e.

$$B_{eff}(\vec{k}) = \sum_{i} B_{eff}^{0i}\ \exp[\ i\vec{k}.\vec{R}_{0i}]$$

$$= B(\vec{k}) + \sum_{i \in \mathbb{C}} b^{0i}\ \exp[\ i\vec{k}.\vec{R}_{0i}]\ . \qquad (3.70)$$

We also note that,

$$b^{ji} = (\ b^{ij})^T, \qquad (3.71)$$

and, therefore, we need to solve Eq. (3.67) for $j > i$ only. This reduces the number of self-consistent coupled equations in Eqs. (3.66) and (3.67) to $[\ m(m-1)/2\ ] + 1$. This number can be further reduced by exploiting the symmetry of the cluster. Note that, all these equations involve matrices of rank

$(l+1)^2$, where $l$ is the maximum number of angular momentum
states used in evaluating the phase-shifts. Therefore, with
the modern computers, solving KKR-CCPA equations for a 5-site
cluster (for which there are 11 coupled equations) will not
be difficult at all.

A cluster consisting of a central site and its shell of
nearest neighbors should be the ideal choice. But it will be
computationally demanding and so we propose an alternative,
though approximate method. A nearest-neighbor cluster has
the rotational symmetry of the lattice. Thus, one can take a
two-atom cluster consisting of the central site ( site 0) and
one of its nearest neighbors (say, site 1). The KKR-CCPA
equations for a two-atom cluster, are given in Chapter 4. By
solving these equations, one can obtain $C_{eff}$ and $b^{01}$. And
then, $b^{0m}$, for the rest of the nearest neighbors, can be
found by rotational symmetry, since, $b^{ij}$ will transform like
$B^{ij}$. These $b^{0i}$, can then be used in Eq. (3.70).

Note that, as in the KKR-CPA, the first-order
correction to the KKR-CCPA inverse t-matrices is of the order
of $\omega^2 = xy \, (\delta C)^2$. This implies that, the KKR-CCPA, like the
KKR-CPA, is exact in the limit of vanishing concentration of
either constituent and also, in the limit when the difference
between the two atoms is small.

## 3.4 THE CONFIGURATION AVERAGED GREEN'S FUNCTION

The Green's functions for site-diagonal (SD) and non-site-diagonal (NSD) cases can be written from Eq. (3.10) as[12]

$$G_{SD}(\vec{r},\vec{r}') = Tr\left[ T^{ii} F^i(\vec{r}_i ,\vec{r}'_i) \right] - \sum_L Z_L^i(\vec{r}_i) J_L^i(\vec{r}'_i), \qquad (3.72)$$

and

$$G_{NSD}(\vec{r},\vec{r}') = Tr\left[ T^{ij} F^{ji}(\vec{r}_i ,\vec{r}'_j) \right], \qquad (3.73)$$

where, Tr stands for trace over the angular momentum index L, and

$$F_{LL'}^i(\vec{r}_i ,\vec{r}'_i) = Z_L^i(\vec{r}_i) Z_{L'}^i(\vec{r}'_i), \qquad (3.74)$$

and

$$F_{LL'}^{ji}(\vec{r}_i ,\vec{r}'_j) = Z_L^j(\vec{r}'_j) Z_{L'}^i(\vec{r}_i). \qquad (3.75)$$

Configuration averaging Eqs. (3.72) and (3.73), we get

$$\langle G_{SD}(\vec{r},\vec{r}')\rangle = Tr\langle T^{ii}F^i(\vec{r}_i ,\vec{r}'_i)\rangle - \sum_L \langle Z_L^i(\vec{r}_i)J_L^i(\vec{r}'_i)\rangle, \qquad (3.76)$$

and

$$\langle G_{NSD}(\vec{r},\vec{r}')\rangle = Tr \langle T^{ij}F^{ji}(\vec{r}_i ,\vec{r}'_j) \rangle. \qquad (3.77)$$

The second term in Eq. (3.76) can be evaluated directly. The joint averages appearing in Eqs. (3.76) and (3.77) are of

the form $\langle T^{11} U^i \rangle$ and $\langle T^{ij} U^{ji} \rangle$. These can be found by the augmented space method,[89] if we can express them in terms of the random variables $n_i$ defined in Eq. (2.32). We write,

$$U^i = U^B + \delta U \, n_i \tag{3.78}$$

and

$$U^{ji} = U^{BB} + U_1 \, n_i \, n_j + U_2 \, n_i + U_3 \, n_j \,, \tag{3.79}$$

where,

$$\delta U = U^A - U^B, \tag{3.80}$$

$$U_1 = U^{AA} + U^{BB} - U^{AB} - U^{BA},$$

$$U_2 = U^{AB} - U^{BB}, \tag{3.81}$$

and

$$U_3 = U^{BA} - U^{BB}.$$

## (A) Determination of $\langle T^{ii} U^i \rangle$.

Using Eq. (3.78), we can write

$$\langle T^{ii} U^i \rangle = \langle T^{ii} \rangle U^B + \langle T^{ii} n_i \rangle \, \delta U$$

$$= T^{oo}_{eff} U^B + \langle T^{ii} n_i \rangle \, \delta U. \tag{3.82}$$

By augmented space theorem,[52] we can write

$$\langle T^{ii} n_i \rangle = \langle i;f | \left[ \tilde{A}(\{M^i\}) \right]^{-1} M^i | i;f \rangle, \tag{3.83}$$

where $\tilde{A}(\{M^i\})$ is given by Eq. (3.26). Using Eq. (3.44a), we get,

$$\langle T^{ii} n_i \rangle = x \langle i;f | \tilde{A}^{-1} | i;f \rangle + (xy)^{1/2} \langle i;f | \tilde{A}^{-1} | i;f_i \rangle.$$

But, by augmented space theorem,

$$\langle i;f | \tilde{A}^{-1} | i;f \rangle = \langle T^{ii} \rangle = T^{oo}_{eff} \, ,$$

so that, we have,

$$\langle T^{ii} n_i \rangle = x \, T^{oo}_{eff} + (xy)^{1/2} \langle i;f | \tilde{A}^{-1} | i;f_i \rangle. \tag{3.84}$$

Substituting Eq. (3.84) in Eq. (3.82) we get,

$$\langle T^{ii} U^i \rangle = T^{oo}_{eff} \bar{U} + (xy)^{1/2} \langle i;f | \tilde{A}^{-1} | i;f_i \rangle \, \delta U, \tag{3.85}$$

where

$$\bar{U} = x \, U^A + y \, U^B. \tag{3.86}$$

The only unknown term in Eq. (3.85) is $\langle i;f| \underset{\sim}{A}^{-1} |i:f_i\rangle$. It can be found within the KKR-CCPA by following the procedure outlined in the preceding section. After the first partitioning of the augmented space, we get,

$$\langle i;f| \underset{\sim}{A}^{-1} |i;f_i\rangle = \langle i;f| \hat{A}^{-1} |i;f_i\rangle, \qquad (3.87)$$

where $\hat{A}$ is given by Eq. (3.38). After the second partitioning in the scheme of eq. (3.39), $\langle i;f| \underset{\sim}{A}^{-1} |i;f_i\rangle$ falls in the top right-hand side block of $\hat{A}^{-1}$, i.e. if we partition $\hat{A}^{-1}$ as,

$$\hat{A}^{-1} = \begin{pmatrix} E_1 & \vdots & E_{12} \\ \cdots & \vdots & \cdots \\ E_{21} & \vdots & E_2 \end{pmatrix}, \qquad (3.88)$$

then $\langle i;f| \hat{A}^{-1} |i;f_i\rangle$ will fall in $E_{12}$ block, which by partition theorem, is given by

$$E_{12} = - \left[ \mathscr{A}_1 - \mathscr{A}_{12} \mathscr{A}_2^{-1} \mathscr{A}_{21} \right]^{-1} \mathscr{A}_{12} \mathscr{A}_2^{-1}, \qquad (3.89)$$

where the matrices appearing on the right-hand side are given by Eqs. (3.47) to (3.50). With the help of Eq. (3.54), we can write Eq. (3.89) as

$$\langle i;f| \hat{A}^{-1} |i;f_i\rangle = - \langle i;f| \left[ \mathscr{A}_1 - \omega \,\Gamma\, \omega \right]^{-1} \mathscr{A}_{12}\, \mathscr{A}_2^{-1} |i;f_i\rangle$$

$$= - \sum_{j,k} \sum_{f_\sigma} \sum_{f_{\sigma'}} \left[ \langle i;f| \left( \mathscr{A}_1 - \omega \,\Gamma\, \omega \right)^{-1} |j;f_\sigma\rangle \langle j;f_\sigma|\mathscr{A}_{12}|k;f_{\sigma'}\rangle \right.$$

$$\left. \times \langle k;f_{\sigma'}, |\mathscr{A}_2^{-1}|i;f_i\rangle \right]. \tag{3.90}$$

From Eq. (3.48), we have

$$\langle j;f_\sigma|\mathscr{A}_{12}|k;f_{\sigma'}\rangle = \omega \,\delta_{jk}\, \delta_{\sigma\omega}\, \delta_{k\sigma'}, \tag{3.91}$$

and thus, Eq. (3.90) can be rewritten as

$$\langle i;f| \hat{A}^{-1} |i;f_i\rangle = - \sum_{j} \left[ \langle i;f| \left( \mathscr{A}_1 - \omega \,\Gamma\, \omega \right)^{-1} |j;f\rangle \,\omega \right.$$

$$\left. \times \langle j;f_j| \mathscr{A}_2^{-1} |i;f_i\rangle \right]. \tag{3.92}$$

From Eq. (3.57), we have

$$\langle i;f| \left( \mathscr{A}_1 - \omega \,\Gamma\, \omega \right)^{-1} |j;f\rangle = T_{\text{eff}}^{ij}, \tag{3.93}$$

and from Eqs. (3.66) and (3.67) we have

$$\langle j;f_j| \mathscr{A}_2^{-1} |i;f_i\rangle = \omega^{-1} \left[ (\overline{C} - C_{\text{eff}})\, \delta_{ij} + b^{ji} \,(1 - \delta_{ij}) \right] \omega^{-1} \tag{3.94}$$

Substituting Eqs. (3.93) and (3.94) in Eq. (3.92) we get

$$\langle i;f| \hat{A}^{-1} |i;f_i\rangle = T_{eff}^{oo} (C_{eff} - \bar{C}) \omega^{-1} - \sum_{j\in\mathbb{C}} T_{eff}^{ij} b^{ji} \omega^{-1}.$$

(3.95)

Thus, from Eq. (3.85) we finally get

$$\langle T^{ii} U^i\rangle = T_{eff}^{oo}\left[ \bar{U} + (C_{eff} - \bar{C}) (\delta C)^{-1} \delta U \right] -$$
$$\sum_{j\in\mathbb{C}} T_{eff}^{ij} b^{ji} (\delta C)^{-1} \delta U.$$

(3.96)

We note that,

$$\langle T^{ii} U^i\rangle \neq \langle T^{ii}\rangle\langle U^i\rangle,$$

(3.97)

which is true within the single-site KKR-CPA as well.[6,64] In Chapter 4, we will show that, if we take a one-atom cluster, Eq. (3.96) exactly reduces to that obtained by the restricted averaging method within the KKR-CPA.

Also, we note that, the expression for the joint average within the KKR-CCPA given in Ref. 64 (Eq. (16b) of that paper) is not correct, because, in that expression the second term of Eq. (3.96) is missing. However, within the single-site KKR-CPA, it is exactly the same as Eq. (3.96).[88]

(B) Determination of $\langle T^{ij} U^{ji} \rangle$.

Using Eqs. (3.79) and (3.81) we can write

$$\langle T^{ij} U^{ji} \rangle = T^{ij}_{eff} U^{BB} + \langle n_i T^{ij} n_j \rangle U_1 + \langle n_i T^{ij} \rangle U_2 + \langle T^{ij} n_j \rangle U_3.$$

$$(3.98)$$

Let us determine the terms in Eq. (3.98) separately. By augmented space theorem we have

$$\langle n_i T^{ij} \rangle = \langle i;f| \; M^i \left[ \tilde{A}(\{M^i\}) \right]^{-1} |j;f \rangle. \qquad (3.99)$$

Using (3.44a), we can rewrite Eq. (3.99) as

$$\langle n_i T^{ij} \rangle = x \; T^{ij}_{eff} + (xy)^{1/2} \langle i;f_i| \; \tilde{A}^{-1} |j;f \rangle. \qquad (3.100)$$

In a similar manner, we can write

$$\langle T^{ij} n_j \rangle = x \; T^{ij}_{eff} + (xy)^{1/2} \langle i;f| \; \tilde{A}^{-1} |j;f_j \rangle. \qquad (3.101)$$

Also, we can write

$$\langle n_i T^{ij} n_j \rangle = \langle i;f| \; M^i \left[ \tilde{A}(\{M^i\}) \right]^{-1} M^j |j;f \rangle. \qquad (3.102)$$

Using Eq. (3.44a), one easily gets,

$$\langle n_i T^{ij} n_j \rangle = x^2 \, T_{eff}^{ij} + x(xy)^{1/2} \left[ \langle i;f| \, \tilde{A}^{-1} \, |j;f_j\rangle + \right.$$

$$\left. \langle i;f_i| \, \tilde{A}^{-1} \, |j;f\rangle \right] + xy \, \langle i;f_i| \, \tilde{A}^{-1} \, |j;f_j\rangle. \qquad (3.103)$$

Putting Eqs. (3.100), (3.101), and (3.103) in Eq. (3.98) we get,

$$\langle T^{ij} \, U^{ji} \rangle = T^{ij} \, \overline{\overline{U}} + (xy)^{1/2} \left[ \langle i;f| \, \tilde{A}^{-1} \, |j;f_j\rangle \, (x \, U_1 + U_3) + \right.$$

$$\left. \langle i;f_i| \, \tilde{A}^{-1} \, |j;f\rangle \, (x \, U_1 + U_2) \right] + xy \, \langle i;f_i| \, \tilde{A}^{-1} \, |j;f_j\rangle U_1 \, ,$$

$$(3.104)$$

where

$$\overline{\overline{U}} = x^2 \, U^{AA} + y^2 \, U^{BB} + xy \, U^{AB} + xy \, U^{BA}. \qquad (3.105)$$

The element $\langle i;f| \, \tilde{A}^{-1} \, |j;f_j\rangle$ will fall on $E_{12}$ block of Eq. (3.88), and therefore, it can be written as

$$\langle i;f| \, \tilde{A}^{-1} \, |j;f_j\rangle = - \langle i;f| \left[ \mathscr{A}_1 - \omega \, \Gamma \, \omega \right]^{-1} \mathscr{A}_{12} \, \mathscr{A}_2^{-1} \, |j;f_j\rangle$$

$$= - \sum_{k,l} \sum_{f_\sigma} \sum_{f_{\sigma'}} \left[ \langle i;f| \left( \mathscr{A}_1 - \omega \, \Gamma \, \omega \right)^{-1} |k;f_\sigma\rangle \langle k;f_\sigma| \mathscr{A}_{12} |l;f_{\sigma'}\rangle \right.$$

$$\left. x \, \langle l;f_{\sigma'} |\mathscr{A}_2^{-1}| j;f_j\rangle \right]. \qquad (3.106)$$

Using Eq. (3.91) we get

$$\langle i;f| \tilde{A}^{-1} |j;f_j\rangle = - \sum_k \langle i;f| \left[\mathscr{A}_1 - \omega\, \Gamma\, \omega\right]^{-1} |k;f\rangle\, \omega$$

$$x\, \langle k;f_k|\mathscr{A}_2^{-1}|j;f_j\rangle$$

$$= - \sum_k T_{eff}^{ik}\, \omega\, \langle k;f_k|\mathscr{A}_2^{-1}|j;f_j\rangle. \qquad (3.107)$$

Using Eq. (3.94) in Eq. (3.107) one finally gets

$$\langle i;f| \tilde{A}^{-1} |j;f_j\rangle = T_{eff}^{ij}\, (C_{eff} - \bar{C})\, \omega^{-1} - \sum_k T_{eff}^{ik}\, b^{kj}\, \omega^{-1}.$$

$$(3.108)$$

In a similar manner we can obtain

$$\langle i;f| \tilde{A}^{-1} |j;f_j\rangle = \omega^{-1}\, (C_{eff} - \bar{C})\, T_{eff}^{ij} - \sum_k \omega^{-1}\, b^{ik}\, T_{eff}^{kj} .$$

$$(3.109)$$

The element $\langle i;f_i| \tilde{A}^{-1} |j;f_j\rangle$ falls on $E_{22}$ block of Eq. (3.88), which is obtained by partition theorem, as

$$E_{22} = \mathscr{A}_2^{-1} - E_{21}\, \mathscr{A}_{12}\, \mathscr{A}_2^{-1}. \qquad (3.110)$$

Thus, we have,

$$\langle i;f_i| \overset{\sim}{A}^{-1} |j;f_j\rangle = \langle i;f_i| \mathscr{A}_2^{-1}|j;f_j\rangle - \sum_{k,l} \sum_{f_\sigma} \sum_{f_{\sigma'}} \Big[ \langle i;f_i|E_{21}$$

$$|k;f_\sigma\rangle \langle k;f_\sigma|\mathscr{A}_{12}|l;f_{\sigma'}\rangle\langle l;f_{\sigma'}|\mathscr{A}_2^{-1}|j;f_j\rangle \Big] . \qquad (3.111)$$

Using Eqs. (3.67) and (3.91) and a little algebraic manipulation we get,

$$\langle i;f_i| \overset{\sim}{A}^{-1} |j;f_j\rangle = \omega^{-1} b^{ij} \omega^{-1} - \langle i;f_i|E_{12}|j;f\rangle (\bar{C} - C_{eff}) \omega^{-1}$$

$$- \sum_k \langle i;f_i|E_{12}|k;f\rangle b^{kj} \omega^{-1} . \qquad (3.112)$$

From Eq. (3.89) we get

$$\langle i;f_i|E_{12}|k;f\rangle = \omega^{-1} (C_{eff} - \bar{C}) T_{eff}^{ik} - \sum_l \omega^{-1} b^{il} T_{eff}^{lj} .$$

$$(3.113)$$

Therefore, all the terms of Eqs. (3.104) are determined through Eqs. (3.107), (3.108), (3.112), and (3.113). The configuration averaged Green's function,[88] for site-diagonal and non-site-diagonal cases can be obtained from Eqs. (3.96) and (3.104) by substituting $F^i(\vec{r}_i ,\vec{r}_i')$ and $F^{ij}(\vec{r}_i ,\vec{r}_j')$ for $U^i$ and $U^{ij}$.

The configuration averaged density of states is given by

$$\langle n(E) \rangle = - \frac{1}{\pi} \; \text{Im} \int_{\Omega_i} \langle G_{SD}(\vec{r}_i, \vec{r}_i) \rangle \; d\vec{r}_i \qquad (3.114)$$

where the integration is over the central (i-th) Wigner-Seitz cell. The configuration averaged charge density is

$$\langle \rho(\vec{r}) \rangle = - \frac{1}{\pi} \; \text{Im} \int_{-\infty}^{E_F} \langle G_{SD}(\vec{r}, \vec{r}) \rangle \; d\vec{r}. \qquad (3.115)$$

The site-diagonal form of the configuration averaged Green's function[88] is given by,

$$\langle G_{SD}(\vec{r}, \vec{r}') \rangle = \text{Tr} \Bigg[ T_{eff}^{oo} \Big\{ \bar{F}(\vec{r}, \vec{r}') + (C_{eff} - \bar{C})(\delta C)^{-1} \delta F(\vec{r}, \vec{r}') \Big\} -$$

$$\sum_{\in \mathbb{C}} T_{eff}^{ij} \; b^{ji} \; (\delta C)^{-1} \; \delta F(\vec{r}, \vec{r}') -$$

$$\sum_{L} \Big[ x \; Z_L^A(\vec{r}) \; J_L^A(\vec{r}') + y \; Z_L^B(\vec{r}) \; J_L^B(\vec{r}') \Big] \Bigg], \qquad (3.116)$$

where

$$\bar{F}(\vec{r}, \vec{r}') = x \; F^A(\vec{r}, \vec{r}') + y \; F^B(\vec{r}, \vec{r}'), \qquad (3.117)$$

and

$$\delta F(\vec{r}, \vec{r}') = F^A(\vec{r}, \vec{r}') - F^B(\vec{r}, \vec{r}'). \qquad (3.118)$$

In calculating the local properties, such as the component densities of states and component charge densities, one needs the restricted averaged Green's function. The component charge densities are essential for a charge self-consistent implementation of the KKR-CCPA, within the local density approximation of the density functional theory. The restricted averaged Green's function can be determined by embedding a real atom in the effective medium. We will discuss the problem of embedding in the next section.

## 3.5 EMBEDDING A REAL CLUSTER IN THE EFFECTIVE MEDIUM

Several authors have discussed the problem of embedding a cluster of real atoms in an effective medium.[47,60,90,91] Gonis et al[60] have discussed how to embed a real cluster in an effective medium, determined within the KKR-CPA method. The generalization of this technique to an effective medium determined within the KKR-CCPA medium is not straightforward,[67] because, in the KKR-CCPA, the effective t-matrices are no longer site-diagonal. We have, for convenience, clubbed the off-site-diagonal parts of the effective t-matrices ($b^{ij}$) with $B^{ij}$, and have defined a new variable $B^{ij}_{eff}$ . In the discussion that follows Eq. (3.31), we have stressed that, when we embed a cluster of real atoms

in the effective medium, the off-diagonal term between a site inside the cluster (a real atom) and an effective atom, should be $B_{eff}^{ij}$ so as to include correlated scattering between these two sites.[67] Therefore, in the present situation, we assume that, the off-diagonal term between two real atoms be $B^{ij}$, whereas, that between two sites, when at least one of them is an effective site, be $B_{eff}^{ij}$. Admittedly, this is an *ad hoc* prescription and needs further work. In Chapter 4, we will discuss the effect of different choices of the off-diagonal terms (between real and effective atoms) on the density of states.

In the present prescription, the restricted averaged Green's functions, following Ref. 12, can be written as

$$\langle G(\vec{r}, \vec{r}') \rangle_{i=\alpha} = \text{Tr}\left[\langle T^{ii} \rangle_{i=\alpha} F^{\alpha}(\vec{r}_i, \vec{r}_i')\right] + \sum_{L} Z_L^{\alpha}(\vec{r}_i) J_L^{\alpha}(\vec{r}_i')$$

$$(3.119)$$

and

$$\langle G(\vec{r}, \vec{r}') \rangle_{i=\alpha, j=\beta} = \text{Tr}\left[\langle T^{ij} \rangle_{i=\alpha, j=\beta} F^{\beta\alpha}(\vec{r}_i, \vec{r}_j')\right], \quad (3.120)$$

where $\alpha, \beta$ = A or B. The restricted averaged path-operators can be found by a simple partitioning technique,[12] to give

$$\langle T^{ii} \rangle_{i=\alpha} = D^{\alpha} T_{eff}^{oo}, \qquad (3.121)$$

and

$$\langle T^{ij} \rangle_{i=\alpha, j=\beta} = D^{\alpha} T_{eff}^{ij} \left[ I - (C^{\beta} - C_{eff}) D^{\beta} T_{eff}^{j1} \right.$$

$$\left. (C^{\alpha} - C_{eff}) D^{\alpha} T_{eff}^{ij} \right]^{-1} D^{\beta \dagger}, \qquad (3.122)$$

where

$$D^{\alpha} = \left[ I + T_{eff}^{00} ( C^{\alpha} - C_{eff} ) \right]^{-1}. \qquad (3.123)$$

The component density of states for an $\alpha$-type atom is given by

$$n^{\alpha}(E) = - \frac{1}{\pi} \text{Tr Im} \left[ D^{\alpha} T_{eff}^{oo} \int_{\Omega_n} F^{\alpha}(\vec{r}_n, \vec{r}_n) \, d\vec{r}_n \right]. \qquad (3.124)$$

The component charge density $\rho^{(\alpha)}(\vec{r})$ on an $\alpha$-type atom is given by[92]

$$\rho^{\alpha}(\vec{r}) = - \frac{1}{\pi} \text{Tr Im} \left[ D^{\alpha} T_{eff}^{oo} \int_{-\infty}^{E_F} F^{\alpha}(\vec{r}, \vec{r}) \, dE \right]. \qquad (3.125)$$

One can construct the potentials $v_{\alpha}(\vec{r})$ from $\rho^{\alpha}(\vec{r})$ using the local density approximation of the density functional theory,[13-15] and hence, can achieve charge self-consistency. The methodology is as follows. One starts off with the potentials $v_{\alpha}(\vec{r})$ of the pure $\alpha$-type solid ( $\alpha$ = A or B), and then solves the KKR-CCPA equations given by Eqs. (3.66) and (3.67). From Eq. (3.125), one calculates the component charge densities, which are used to calculate new potentials

$v_\alpha(\vec{r})$. These new potentials are again used to solve the KKR-CCPA equations. This procedure is continued till the charge densities in the successive iterations become consistent. Therefore, this method is independent of initial parameters.

Note that, if we average Eq. (3.124) over the configurations of the n-th site, it would not be identical to Eq. (3.114).[88] This is expected, because, Eq. (3.114) is derived by averaging over all the configurations of the cluster. For a one-atom cluster, both these equations, though derived through quite different techniques, are exactly identical. We may stress that, while calculating the averaged properties of an alloy within the KKR-CCPA, Eqs. (3.114) and (3.115) should be used rather than averaging Eqs. (3.124) and (3.125). However, Eqs. (3.124) and (3.125) are, nevertheless important, when one needs the local properties, such as the component density of states and component charge densities.

If we embed two impurities of type $\alpha$ and $\beta$ on the sites i and j respectively, the local density of states on the respective sites is given by

$$n_2^\alpha (E) = - \frac{1}{\pi} \text{Tr Im} \left[ \langle T^{ii} \rangle_{i=\alpha, j=\beta} F^\alpha \right], \qquad (3.126)$$

and

$$n_2^\beta (E) = - \frac{1}{\pi} \text{Tr Im} \left[ \langle T^{jj} \rangle_{i=\alpha, j=\beta} F^\beta \right]. \qquad (3.127)$$

Hence, we need only to find the path operator matrices $\langle T^{ii}\rangle_{i=\alpha,\,j=\beta}$ and $\langle T^{jj}\rangle_{i=\alpha,\,j=\beta}$. It is straightforward to obtain these matrices by the partitioning technique.[12] The real space is divided into two sub-spaces; one for the impurity sites and the other for the rest effective medium. Then by simple matrix algebra one easily gets

$$\langle T^{ii}\rangle_{i=\alpha,\,j=\beta} = \left[\left(T^{oo}_{eff} - T^{ij}_{eff}\,(c^{\beta} - c_{eff})\,D^{\beta}\,T^{ji}_{eff}\right)^{-1} + (c^{\alpha} - c_{eff})\right]^{-1}, \qquad (3.128)$$

and

$$\langle T^{jj}\rangle_{i=\alpha,\,j=\beta} = \left[\left(T^{oo}_{eff} - T^{ji}_{eff}\,(c^{\alpha} - c_{eff})\,D^{\alpha}\,T^{ij}_{eff}\right)^{-1} + (c^{\beta} - c_{eff})\right]^{-1}, \qquad (3.129)$$

Eqs. (3.124) to (3.129) can be used to calculate local density of states and charge densities for a single impurity or two impurities of a foreign kind as well.


## 3.6 CONCLUSION

In this chapter we showed that, one can go beyond the CPA in the conventional KKR Green's function formalism by the application of augmented space formalism to the KKR Green's

function. We found that, the KKR-CCPA introduces site-off-diagonal corrections as well in the scattering matrices, along with the usual site-diagonal corrections, which we do not get in a single-site approximation like the KKR-CPA. The KKR-CCPA restores the translational symmetry of the effective medium. The KKR-CCPA formulation has been put on the same rigorous footing as the KKR-CPA, in which one can calculate the density of states, the component density of states, and the charge densities, self-consistently within the local density approximation of the density functional theory. Therefore, our KKR-CCPA formulation is a first-principles parameter-free theory of disordered alloys, which includes correlated scattering from clusters of atoms. In this formulation, we have neglected the short-range order. A formal extension of the present formulation to include the effects of short-range order will be presented in Chapter 5.

# CHAPTER 4
# APPLICATION OF THE KORRINGA-KOHN-ROSTOKER CLUSTER COHERENT-POTENTIAL APPROXIMATION TO A MODEL SYSTEM

## 4.1 INTRODUCTION

The implementation of the Korringa-Kohn-Rostoker cluster coherent-potential approximation (KKR-CCPA) to realistic systems is involved, and is computationally demanding. Therefore, it should be first tested on simple models before a full-fledged realistic implementation is attempted. This formulation has already been applied to an over-simplified s phase-shift model.[65] This model rests on the *ad hoc* assumption that, the shape of the density of states curve is semi-circular. In this chapter, our aim is to apply this formulation to a one-dimensional muffin-tin alloy, for which we do not have to make such assumption.[67] Another advantage of choosing this model is that, for this model, the involved k-space integrations can be obtained analytically,[69] which greatly reduces the computational effort.

In section 4.2, we describe the one-dimensional muffin-tin alloy model. We have calculated the density of states for this model using the KKR-CCPA formulation for one-atom and two-atom clusters. In section 4.3, we outline the

methodology of implementing KKR-CCPA for one-atom and two-atom clusters respectively. It is found that, for a one-atom cluster, the KKR-CCPA equations reduce exactly to the familiar KKR-CPA equation, which is the correct limit.[67] Also, we show that, the expression for the configuration averaged Green's function for a one-atom cluster reduces exactly to that, what one would get by the restricted averaging method in the KKR-CPA. In section 4.4, we present the results of our calculations of density of states within the KKR-CCPA. We observe that, the KKR-CCPA density of states is somewhat structured in comparison to the KKR-CPA density of states. We show that, the structures in the KKR-CCPA density of states are close to the structures in the local density of states on the impurities embedded in the KKR-CPA effective medium. This suggests that, the structures in the KKR-CCPA density of states are due to correlated scattering from clusters of atoms. Also, we present the averaged density of states on the central site of a cluster of atoms embedded in the KKR-CPA medium, for clusters of 2, 3, and 5 atoms respectively. These calculations are similar to those proposed by Gonis $et$ $al.$[60] We find that, this averaged density of states reproduces some of the structures of the KKR-CCPA density of states, which become prominent as we increase the cluster-size. In section 4.5, we give our conclusions.

## 4.2 THE ONE-DIMENSIONAL MODEL

We consider a one-dimensional alloy of non-overlapping muffin-tin potentials described by the Hamiltonian[69]

$$H = -\frac{d^2}{dx^2} + \sum_n v_n(x - na) = -\frac{d^2}{dx^2} + \sum_n v_n(x_n). \qquad (4.1)$$

In close analogy with the muffin-tin model in three dimensions we assume that $v_n(x)$ is symmetric in x and vanishes for $|x| \geq r_M$ (the muffin-tin radius), $r_M \leq a/2$ (a is the lattice constant). Due to this symmetry, various quantities, such as the t-matrices and wave functions, can be expanded in terms of symmetric and anti-symmetric functions[69] defined as:

$$Y_0(\hat{x}) = 1/\sqrt{2},$$

and $(4.2)$

$$Y_1(\hat{x}) = 1/\sqrt{2} \, \text{sign}(x).$$

These functions are analogous to the spherical harmonics in three dimensions. The one-dimensional analog of the spherical Bessel and Hankel functions are defined as,[69]

$$j_l(z) = \cos(z - l\pi/2), \quad l = 0, 1,$$

and $(4.3)$

$$h_l(z) = \exp[iz - l\pi/2], \quad l = 0, 1.$$

Almost all of the familiar identities involving spherical Bessel functions and spherical harmonics have one-dimensional analogs.[69]

The on-the-energy-shell matrix elements of the single scatterer t-matrix are given by

$$t_{ll'} = - \varkappa \exp[i\theta_l] \sin\theta_l \; \delta_{ll'}, \qquad (4.4)$$

where $\varkappa = \sqrt{E}$ and $\theta_l$ are the phase-shifts. Unlike the case in three dimensions, in this case, we have only two components of $l$, i.e. 0 and 1. The site-diagonal form of the Green's function of this system in real space can be written as,

$$G(x,x') = \sum_{ll'} Z_l(x) \, T_{ll'}^{oo} \, Z_{l'}(x') - \sum_l Z_l(x) \, J_{l'}(x'), \qquad (4.5)$$

where $Z_l(x)$ and $J_l(x)$ are respectively the regular and irregular solutions of the Schrödinger equation for an isolated muffin-tin potential, and are normalized such that, at $r \equiv |x| = r_M$, they join smoothly to

$$Z_l(x) = Y_l(\hat{x}) \left[ j_l(\varkappa r) \, C_l - \frac{i}{\varkappa} \, h_l(\varkappa r) \right], \qquad (4.6)$$

and

$$J_l(x) = Y_l(\hat{x}) \, j_l(\varkappa r), \qquad (4.7)$$

where

$$C_l = 1/t_l \; . \qquad (4.8)$$

In Eq. (4.5), $T_{ll'}^{oo}$, are on-the-energy-shell matrix elements of the path-operator, and for the KKR-CCPA effective medium, it can be written as,

$$T_{eff}^{ij} = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \left[ C_{eff} - B_{eff}(k) \right]^{-1} \exp[ik(i-j)a] , \qquad (4.9)$$

where

$$B_{eff}(k) = B(k) + b^{01} \exp(ika). \qquad (4.10)$$

$B(k)$ are the KKR structure function matrix in one dimension, whose elements are given by[69]

$$B_{ll'}(k) = \frac{1}{N} \sum_{i \neq j} B_{ll'}^{ij} \exp(-ik(i-j)a), \qquad (4.11)$$

where $B_{ll'}^{ij}$ are the real space versions of $B_{ll'}(k)$, and are given by,[69]

$$B^{ij} = \frac{\exp(ik|i-j|a)}{i\varkappa} \begin{pmatrix} 1 & -i \ \text{sign}(i-j) \\ i \ \text{sign}(i-j) & 1 \end{pmatrix} . \qquad (4.12)$$

The indexing of the sites is as follows: the central site is taken as 0-the site, the numbering on the right side is in terms of positive integers, and on the left it is in terms of negative integers. Substituting Eq. (4.12) in Eq. (4.11) we get,[69]

$$B(k) = \frac{1}{i\varkappa} \begin{bmatrix} -1+ \dfrac{i\ \sin(\varkappa a)}{\cos(ka)-\cos(\varkappa a)} & \dfrac{\sin(ka)}{\cos(ka)-\cos(\varkappa a)} \\[4mm] \dfrac{-\sin(ka)}{\cos(ka)-\cos(\varkappa a)} & -1+ \dfrac{i\ \sin(\varkappa a)}{\cos(ka)-\cos(\varkappa a)} \end{bmatrix}.$$

$$(4.13)$$

The inverse of the effective t-matrices, $C_{eff}$ may not be diagonal in angular momentum space, when calculated within the KKR-CCPA.[67] Therefore, we consider a general case, when $C_{eff}$ are not diagonal in $l$-space. Eq. (4.9) can be transformed into a contour integration on a complex z-plane by putting $z = \exp(ika)$:[67]

$$T_{eff}^{ij} = \frac{1}{2\pi i} \oint_C dz\ z^{j-i-1} \frac{g(z)}{\lambda z^4 +\delta z^3 +\alpha z^2 +\beta z +\gamma} , \qquad (4.14)$$

where C is the unit circle centered at $z=0$ and $g(z)$ is a matrix in $l$-space, whose elements are given by

$$g_{00}(z)= (z^2+ 1- 2z \cos(\varkappa a)) [i- \varkappa C_{11}+ \varkappa b_{11} z]+ 2z \sin(\varkappa a),$$

$$g_{11}(z)= (z^2+ 1- 2z \cos(\varkappa a)) [i- \varkappa C_{00}+ \varkappa b_{00} z]+ 2z \sin(\varkappa a),$$

$$(4.15)$$

$$g_{01}(z)= \varkappa( C_{01} - b_{01} z) (z^2+ 1- 2z \cos(\varkappa a))+ z^2- 1 ,$$

and

$$g_{10}(z)= \varkappa( C_{10} - b_{10} z) (z^2+ 1- 2z \cos(\varkappa a))- z^2+ 1.$$

Also, we have

$$\lambda = E ( b_{00} b_{11} - b_{01} b_{10} ),$$

$$\delta = \eta - \varkappa (b_{01} - b_{10}) - 2 \lambda \cos(\varkappa a),$$

$$\alpha = \lambda + \gamma + 2\varkappa(C_{01} - C_{10}) - 2 \eta \cos(\varkappa a) ,$$

$$\beta = 2 \cos(\varkappa a) [ 2 - \gamma - \varkappa (C_{01} - C_{10})] + 2\sin(\varkappa a)$$

(4.16)

$$[ 2i - \varkappa (C_{00} + C_{11})] + \eta + \varkappa (b_{01} - b_{10})$$

$$\gamma = E [C_{00} C_{11} - C_{01} C_{10}] - i\varkappa (C_{00} + C_{11}) - \varkappa (C_{01} - C_{10})$$

and

$$\eta = i\varkappa(b_{00} + b_{11}) - E (C_{00}b_{11} + C_{11}b_{00} - C_{01}b_{10} - C_{10}b_{01}).$$

In Eqs. (4.15) and (4.16), $C \equiv C_{eff}$ and $b \equiv b^{01}$; the subscripts are the angular momentum indices.

Now let us consider a system, where the one-dimensional muffin-tin potentials are of the form

$$\upsilon_n(x) = -V_0^{A(B)} \theta(r_M - r).$$

(4.17)

These are potential wells, and the phase-shifts for a single potential can be written as,[93]

$$\theta_l = - \varkappa \, r_M + \tan^{-1}\left[\left(\frac{k_1}{\varkappa}\right)^{-l} \tan(k_1 r_M)\right] \qquad (4.18)$$

where

$$k_1 = \sqrt{E + V_0} \; .$$

The wave functions $Z_l(x)$ inside the muffin-tin cell, normalized such that they match with Eq. (4.6) at $r = r_M$, are given by[93]

$$Z_o(x) = \frac{-1}{\varkappa \, \sin\theta_o} \frac{\cos(\varkappa r_M + \theta_o)}{\cos(k_1 r_M)} \cos(\varkappa r + \theta_o) \, Y_o(\hat{x}), \qquad (4.19)$$

$$Z_1(x) = \frac{-1}{\varkappa \, \sin\theta_1} \frac{\sin(\varkappa r_M + \theta_1)}{\sin(k_1 r_M)} \cos(\varkappa r + \theta_1) \, Y_1(\hat{x}). \qquad (4.20)$$

The density of states can be found as,

$$n(E) = - \frac{1}{\pi} \, \mathrm{Im} \, \mathrm{Tr} \left[ T_{ll'}^{oo}, F_{ll'} \right], \qquad (4.21)$$

where

$$F_{ll'} = \int_{-a/2}^{a/2} Z_l(x) \, Z_{l'}(x) \, dx$$

$$= \frac{\delta_{ll'}}{2E \, \sin^2\theta_l} \left[ \frac{\cos^2(\varkappa r_M + \theta_l - l\pi/2)}{\cos^2(k_1 r_M - l\pi/2)} \left\{ r_M + \frac{\sin(2k_1 r_M - l\pi)}{2k_1} \right\} + \right.$$

$$\left. \frac{a}{2} - r_M + (-1)^l \left( \frac{\sin(\varkappa a + 2\theta_l) - \sin(2\varkappa r_M + 2\theta_l)}{2\varkappa} \right) \right]. \qquad (4.22)$$

The off-diagonal elements of $F$ vanish due to opposite parity of $l = 0$ and $l = 1$ wave functions.[67]

The configuration averaged density of states can be obtained by using Eq. (3.114), and the local density of states can be obtained using Eq. (3.124). However, if we assume that, the off-diagonal term between a real atom and an effective atom is of the form,[67]

$$B_{new}^{ij} = B^{ij} + \mu \, (B_{eff}^{ij} - B^{ij}), \quad 0 \le \mu \le 1, \qquad (4.23)$$

then Eq. (3.124) can not be used to calculate the component density of states. The case $\mu=1$, represents the one which we have adopted in deriving Eq. (3.124). In the present case, the restricted averaged path-operator appearing in Eq. (3.119) can be written as

$$\langle T^{ii} \rangle_{i=\alpha} = (X + P \, W^{-1} \, S)^{-1} \Big[ T_{eff}^{oo} + P \, W^{-1} \, T_{eff}^{10} \Big], \qquad (4.24)$$

where

$$X = I + T_{eff}^{oo} \, (C^{\alpha} - C_{eff}) - T_{eff}^{01} \, b^{10} (1-\mu),$$

$$P = T_{eff}^{oo} \, b^{01} \, (1-\mu),$$

$$\qquad (4.25)$$

$$W = I - T_{eff}^{10} \, b^{01} \, (1-\mu),$$

and

$$S = T_{eff}^{10} \, (C^{\alpha} - C_{eff}) - T_{eff}^{oo} \, b^{10} \, (1-\mu).$$

## 4.3 KKR-CCPA FOR ONE- AND TWO-ATOM CLUSTERS

Let us consider a one-atom cluster consisting of the 0-th site. The configuration space $\phi_0$ for this site is spanned by $|f\rangle = |\nu_0^0\rangle$ and $|f_0\rangle = |\nu_1^0\rangle$. Rewriting Eq. (3.50) for this case, we have

$$\mathscr{A}_2 = (C^B - \mathfrak{X}_1^{oo})|0\rangle\langle 0|\otimes|f_0\rangle\langle f_0| + \delta C |0\rangle\langle 0|\otimes|f_0\rangle\langle f_0|M^o|f_0\rangle\langle f_0| \tag{4.26}$$

where

$$\mathfrak{X}_1^{oo} = \sum_{jk\neq 0} B_{eff}^{oj} T_{eff}^{(o)jk} B_{eff}^{ko} . \tag{4.27}$$

With the help of Eq. (3.44b), Eq. (4.26) reduces to

$$\mathscr{A}_2 = (\tilde{C} - \mathfrak{X}_1^{oo}) |0\rangle\langle 0| \otimes |f_0\rangle\langle f_0|, \tag{4.28}$$

where

$$\tilde{C} = y\, C^A + x\, C^B \tag{4.29}$$

It is evident from Eq. (4.28) that, $\langle i;f_i|\mathscr{A}_2^{-1}|j;f_j\rangle = 0$, for $i \neq j$. Therefore, for a one-atom cluster, the KKR-CCPA equations given by Eq. (3.66) and (3.67) now become

$$C_{eff} = \bar{C} - \omega\, (\tilde{C} - \mathfrak{X}_1^{oo})^{-1}\omega, \tag{4.30}$$

and

$$b^{ij} = 0. \tag{4.31}$$

Thus, predictably, there is no off-diagonal corrections in this case. We note that, for a translationally symmetric effective medium, the site-diagonal path operator can be obtained by a partitioning technique to give,

$$T_{eff}^{oo} = \left[ C_{eff} - \sum_{jk \neq 0} B_{eff}^{o,j} \, T_{eff}^{(o)jk} \, B_{eff}^{ko} \right]^{-1}$$

$$= \left[ C_{eff} - \mathfrak{X}_1^{oo} \right]^{-1}. \qquad (4.32)$$

Eq. (4.32) readily gives us,

$$\mathfrak{X}_1^{oo} = C_{eff} - (T_{eff}^{oo})^{-1}. \qquad (4.33)$$

Putting Eq. (4.33) in Eq. (4.30) we get,

$$C_{eff} = \dot{C} - \omega \left[ \tilde{C} - C_{eff} + (T_{eff}^{oo})^{-1} \right]^{-1} \omega, \qquad (4.34)$$

which readily reduces to the more familiar form of the KKR-CPA equation, which is[8,12]

$$C_{eff} = \bar{C} + (C^A - C_{eff}) \, T_{eff}^{00} \, (C^B - C_{eff}). \qquad (4.35)$$

The site-diagonal form of the configuration averaged Green's function, for this case, can be rewritten from Eq. (3.116) as

$$\langle G_{SD}(r,r')\rangle = \mathrm{Tr}\left[T^{00}_{eff}\left\{\bar{F}(r,r') + (C_{eff} - \bar{C})(\delta C)^{-1}\right.\right.$$

$$\left.\left.\delta F(r,r')\right\}\right] - \sum_{L}\left[x\, Z^{A}_{L}(r)\, J^{A}_{L}(r') + y\, Z^{B}_{L}(r)\, J^{B}_{L}(r')\right]. \quad (4.36)$$

By simple algebraic manipulation one can show that, Eq. (4.36) can be rewritten as,

$$\langle G_{SD}(r,r')\rangle = \mathrm{Tr}\left[x\, D^{A}\, T^{00}_{eff}\, F^{A}(r,r') + y\, D^{B}\, T^{00}_{eff}\, F^{B}(r,r')\right] -$$

$$\sum_{L}\left[x\, Z^{A}_{L}(r)\, J^{A}_{L}(r') + y\, Z^{B}_{L}(r)\, J^{B}_{L}(r')\right]. \quad (4.37)$$

where $D^{A}$ and $D^{B}$ are given by Eq. (3.123). This implies that, within the single-site KKR-CPA, the averaged Green's function obtained by the augmented space formalism is exactly identical to that obtained by the familiar restricted averaging method.

We now consider a two-atom cluster consisting of sites 0 and 1. The configuration space, in this case, is spanned by four vectors, which are $|f\rangle = |v^{o}_{o}\, v^{1}_{o}\rangle$, $|f_{1}\rangle = |v^{o}_{o}\, v^{1}_{1}\rangle$, $|f_{o}\rangle = |v^{o}_{1}\, v^{1}_{o}\rangle$ and $|f_{01}\rangle = |v^{o}_{1}\, v^{1}_{1}\rangle$. The augmented space for the cluster is spanned by eight vectors $|i,f\rangle$, $i = 0, 1$ and $f = f, f_{0}, f_{1}$ and $f_{01}$. For this case, Eq. (3.50) can be rewritten as

$$\mathcal{A}_2 = \left[ \sum_{i=0,1} (C^B - \mathfrak{X}_2^{ii})|i\rangle\langle i| - \sum_{ij=0,1} (B^{ij} + \mathfrak{X}_2^{ij})|i\rangle\langle j| \right] \otimes \sum_{f \neq f} |f\rangle\langle f|$$

$$+ \delta C \sum_{i=0,1} |i\rangle\langle i| \otimes \sum_{f' \neq f} \sum_{f'' \neq f} |f'\rangle\langle f'|M^i|f''\rangle\langle f''|, \qquad (4.38)$$

where

$$\mathfrak{X}_2^{ij} = \sum_{kl \neq 0,1} B_{eff}^{ik} T_{eff}^{(0,1)kl} B_{eff}^{lj} \quad , \text{for } i,j=0,1. \qquad (4.39)$$

It is evident that $\mathfrak{X}_2^{00} = \mathfrak{X}_2^{11}$. Also, it is evident from Eq. (4.38) that, $\mathcal{A}_2$ is a (6x6) matrix. The KKR-CCPA equations, given by Eq. (3.66) and (3.67), now reduce to the following two equations:[67]

$$C_{eff} = \bar{C} - \omega \langle 0;f_0|\mathcal{A}_2^{-1}|0;f_0\rangle \omega = \bar{C} - \omega Q^{00} \omega, \qquad (4.40)$$

and

$$b^{01} = \omega \langle 0;f_0|\mathcal{A}_2^{-1}|1;f_1\rangle \omega = \omega Q^{01} \omega, \qquad (4.41)$$

where

$$Q^{00} = R_6^{-1}. \qquad (4.42)$$

and

$$Q^{01} = R_6^{-1} V^{01} R_5^{-1} \omega R_4^{-1} V^{10} R_3^{-1} \omega R_2^{-1} V^{01} R_1^{-1}. \qquad (4.43)$$

The matrices $R_1$ to $R_6$ are given by

$$R_1 = \tilde{C} - \mathfrak{X}_2^{00},$$

$$R_2 = C - \mathfrak{X}_2^{00} - v^{01} R_1^{-1} v^{10},$$

$$R_3 = \tilde{C} - \mathfrak{X}_2^{00} - \omega R_2^{-1} \omega,$$

$$\quad (4.44)$$

$$R_4 = \tilde{C} - \mathfrak{X}_2^{00} - v^{10} R_3^{-1} v^{01},$$

$$R_5 = \bar{C} - \mathfrak{X}_2^{00} - \omega R_4^{-1} \omega,$$

$$R_6 = \tilde{C} - \mathfrak{X}_2^{00} - v^{01} R_5^{-1} v^{10},$$

$$\quad (4.45)$$

where

$$v^{ij} = B^{ij} + \mathfrak{X}_2^{ij} \;, \text{ for } i, j = 0, 1.$$

The variables $\mathfrak{X}_2^{ij}$ can be found as follows. We partition the effective medium such that, the sites 0 and 1 fall inside the cluster. Now the effective medium path-operators in the cluster subspace can be obtained by solving,[67]

$$\begin{pmatrix} T_{eff}^{00} & T_{eff}^{01} \\ T_{eff}^{10} & T_{eff}^{11} \end{pmatrix} = \left[ \begin{pmatrix} C_{eff} & -B_{eff}^{01} \\ -B_{eff}^{10} & C_{eff} \end{pmatrix} - \begin{pmatrix} \mathfrak{X}_2^{00} & \mathfrak{X}_2^{01} \\ \mathfrak{X}_2^{10} & \mathfrak{X}_2^{11} \end{pmatrix} \right]^{-1}.$$

$$\quad (4.46)$$

Eq. (4.46) readily gives us,

$$\mathfrak{X}_2^{00} = C_{eff} - \left[ T_{eff}^{00} - T_{eff}^{01} (T_{eff}^{00})^{-1} T_{eff}^{10} \right]^{-1}, \qquad (4.47a)$$

$$\mathfrak{X}_2^{01} = - B_{eff}^{01} + \left[ T_{eff}^{00} (T_{eff}^{01})^{-1} T_{eff}^{00} - T_{eff}^{10} \right]^{-1}, \qquad (4.47b)$$

$$\mathfrak{X}_2^{10} = - B_{eff}^{10} + \left[ T_{eff}^{00} (T_{eff}^{10})^{-1} T_{eff}^{00} - T_{eff}^{01} \right]^{-1}. \qquad (4.47c)$$

We may point out that, the effective inverse t-matrices $(C_{eff})$ within the KKR-CCPA may not be diagonal any longer, if the cluster-size is beyond one-atom. Thus, care must be taken when evaluating the path-operators.

## 4.4 RESULTS AND DISCUSSION

In this section we present the results of our calculations of density of states for the one-dimensional muffin-tin alloy described in section 4.2. The lattice parameters (a = 6.00 a.u.) and the muffin-tin radii ($r_m$ = 2.25 a.u.) of the two components of the alloy are taken to be identical. The depth of the two constituent potentials are $V_A$ = -0.3 Ry and $V_B$ = -0.5 Ry respectively. The densities of states for the two pure systems are shown in Fig. 4.1, which show peaks at band edges, characteristics of the
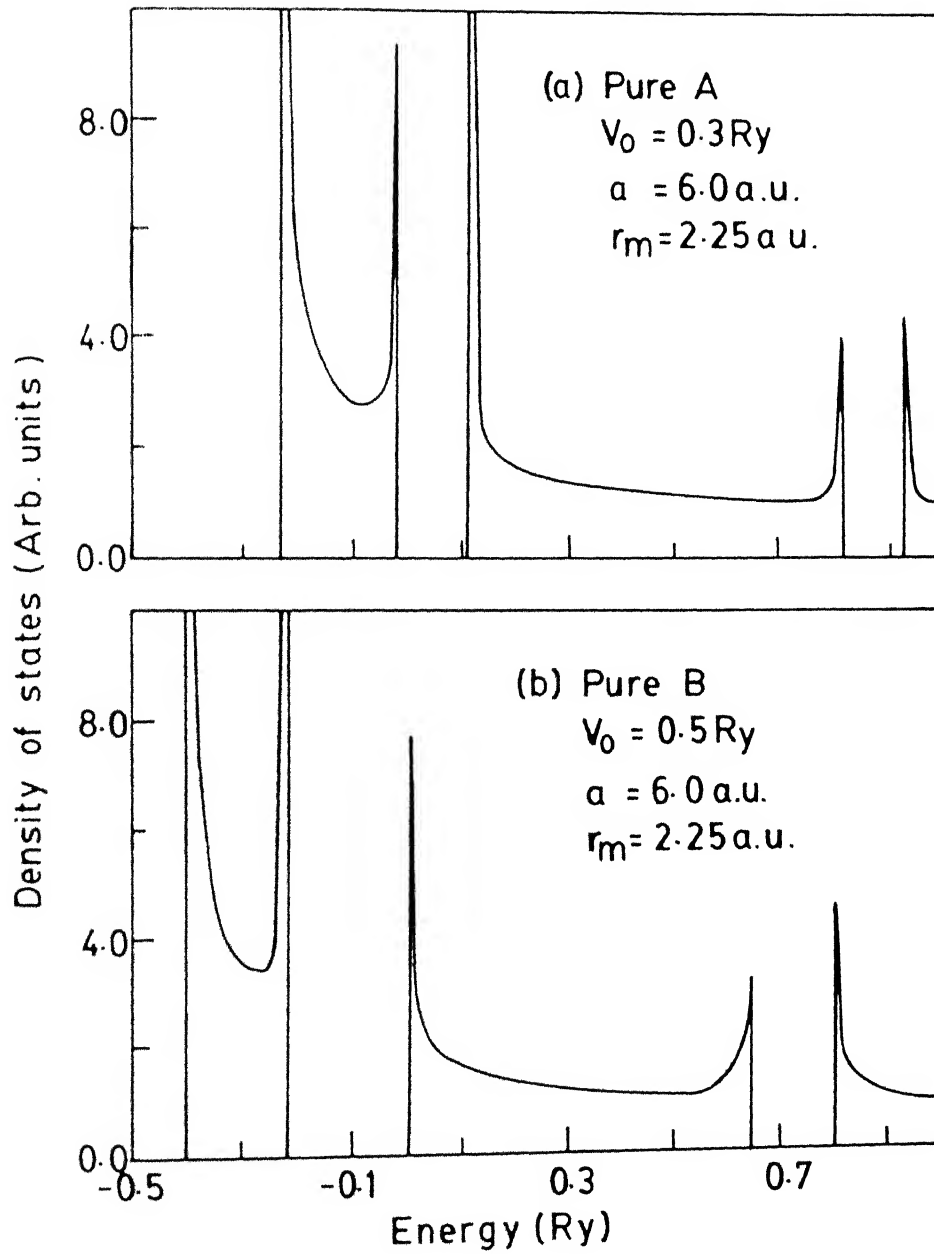
Fig. 4.1 Density of states for the one-dimensional
chain of muffin-tin potentials of depth (a) $V_A$ =
0.3 Ry and (b) $V_B$ = 0.5 Ry. The lattice parameter
and muffin-tin radius are respectively 6.00 a.u
and 2.25 a.u. for both the constituents.

one-dimensional model. For calculating the density of states within the KKR-CCPA, we have taken a two-atom cluster. We have calculated the densities of states for the $A_x B_y$ alloy for two concentrations ($x = 0.1$ and $x = 0.5$).

We first discuss the low concentration limit. Fig. 4.2(a) shows the density of states calculated within the KKR-CPA and KKR-CCPA. We note that, in the first majority band, there is no apparent difference in the KKR-CPA and KKR-CCPA results. However, in the impurity band, there is a noticeable difference between the two. In contrast to a smooth KKR-CPA impurity band centered around $E = -0.14$ Ry, in the KKR-CCPA density of states we observe a shoulder in the KKR-CCPA density of states around $E = -0.16$ Ry and two sharp peaks at $E = -0.12$ Ry and $E = -0.10$ Ry respectively. The extra structures in the KKR-CCPA density of states, seem to arise due to correlated scattering from two-atom clusters. This becomes clear by a close inspection of the local density of states on impurities for a two-impurity cluster embedded in the effective medium. In Fig. 4.2(b), we show the local density of states on A-type impurities embedded in a pure B-medium. We observe that the two-impurity levels at $E = -0.19$ Ry and $E = -0.10$ Ry are close enough to the structures in the minority band of the KKR-CCPA density of states. The sharp structure at $E = -0.12$ Ry in the KKR-CCPA density of states is very close to the single-impurity level at $E =$
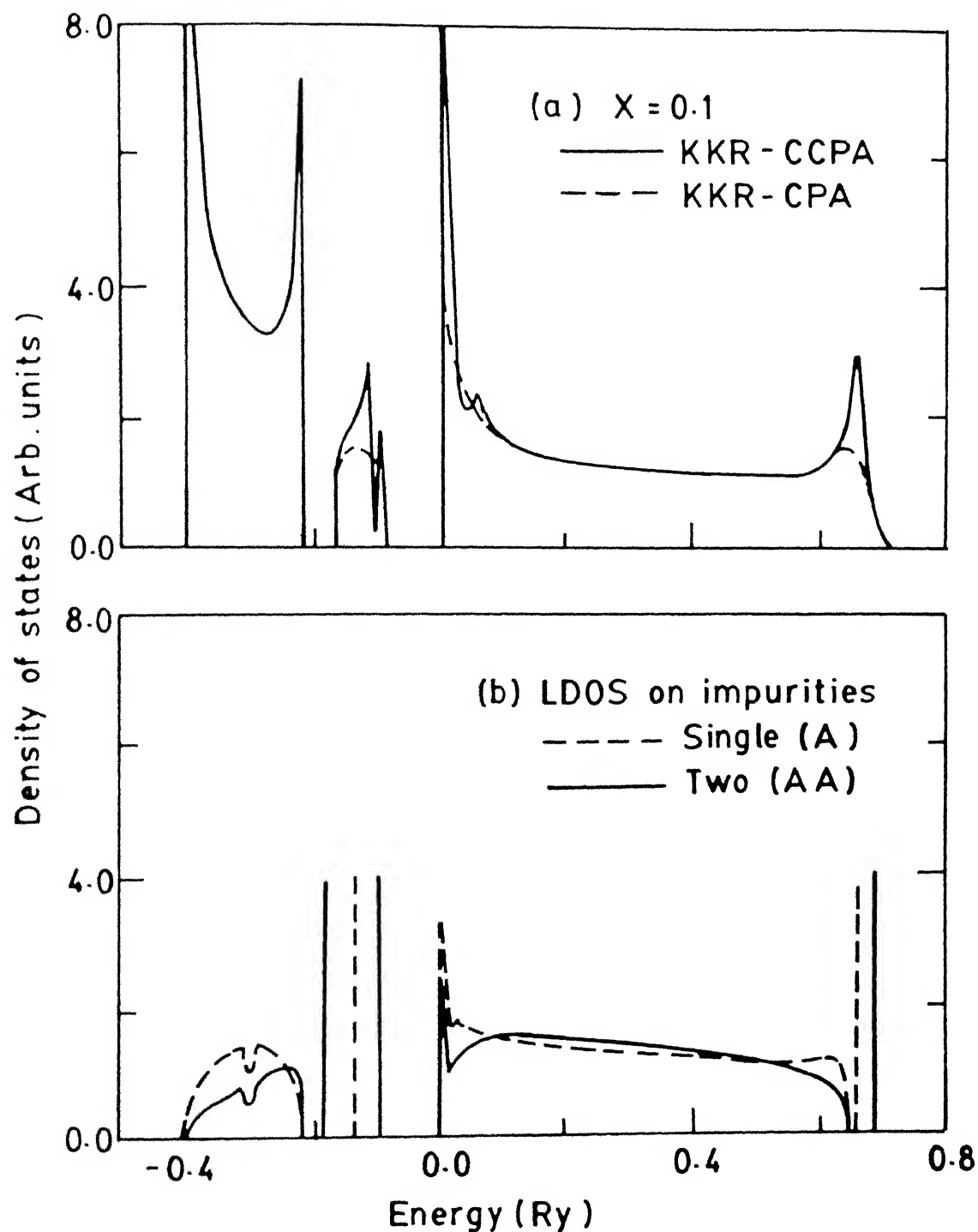
Fig. 4.2 (a) KKR-CPA (dashed line) and KKR-CCPA (solid line) density of states for the alloy with concentration x = 0.1. (b) Local density of states on the impurity site for a single (dashed line) and two (solid line) impurities of type A embedded in the pure B medium.

-0.13 Ry. We also show the local density of states on impurities embedded in the KKR-CPA medium in Figs. 4.3(a) and 4.3(b). If we look at the local density of states on an A-type impurity of an AA-type cluster, as shown in Fig. 4.3(a), we observe that its impurity band is almost identical to that of the KKR-CCPA density of states. The only difference is that in the KKR-CCPA density of states we have an extra structure at $E = -0.12$ Ry, which is very close to the peak at $E = -0.13$ Ry in the local density of states on the A-type impurity of an AB-type cluster, as shown in Fig. 4.3(b). Also, a small but observable structure at $E = 0.06$ Ry in the KKR-CCPA density of states is very close to the two kinks around $E = 0.04$ Ry, in the local density of states on both A-type and B-type impurities of an AB-type cluster, as shown in Fig. 4.3(b). The above discussion suggests that the structures in the KKR-CCPA density of states are due to the correlated scattering from two-atom clusters.

We have also compared our KKR-CCPA results with some calculations obtained by using the embedded cluster method of Gonis *et. al.*[60] We have embedded clusters of two, three, and five atoms in the KKR-CPA medium for $x = 0.1$. The averaged density of states on the central site of the cluster is obtained by calculating the local density of states on the central site for all possible configurations of the cluster and then taking the weighted average. This averaged density
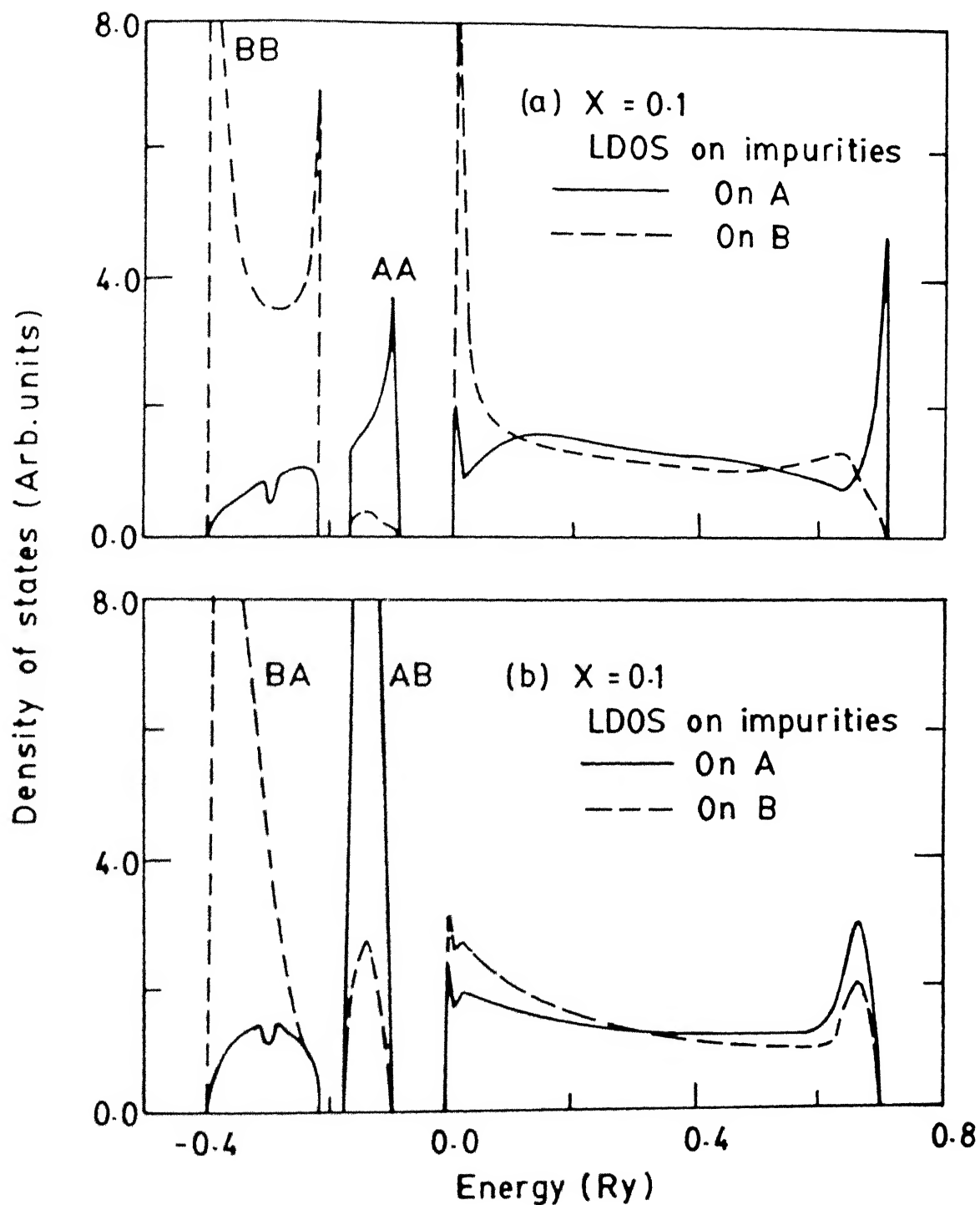
Fig. 4.3 (a) Local density of states on the impurity site for a cluster of two impurities of AA (solid line) and BB (dashed line) type embedded in the KKR-CPA medium for x = 0.1. (b) Local density of states on the impurity site of A (solid line) and B (dashed line) type of an AB-type cluster embedded in the KKR-CPA medium for x = 0.1.

of states produces some of the structures of the KKR-CCPA density of states. In Figs. 4.4(a), 4.4(b), and 4.4(c), we show the averaged density of states, for different cluster sizes. We observe that, for a two-atom cluster, the averaged density of states does not produce the structures of the KKR-CCPA density of states. However, as we increase the cluster-size, the structures in the averaged density of states become prominent, and show resemblance to the KKR-CCPA results. The structure at $E = -0.12$ in the KKR-CCPA density of states is clearly reproduced when the cluster-size is increased to five atoms. This further supports our assertion that the structures in the KKR-CCPA density of states are due to the correlated scattering from clusters of atoms.

In Figs. 4.5(a) and 4.5(b), we show the component density of states and $\ell$-decomposed KKR-CCPA density of states respectively. It is observed from Fig. 4.5(b) that, the lowest band is dominantly $\ell = 0$ in character, while the next higher band is $\ell = 1$ in character.

In Fig. 4.6 we compare the KKR-CCPA density of states and the concentration-weighted average of the component density of states of Fig. 4.5(a). This weighted average is what one would get by the restricted averaging method. It is important to note that these two densities of states are not same. It is expected, since the KKR-CCPA density of states
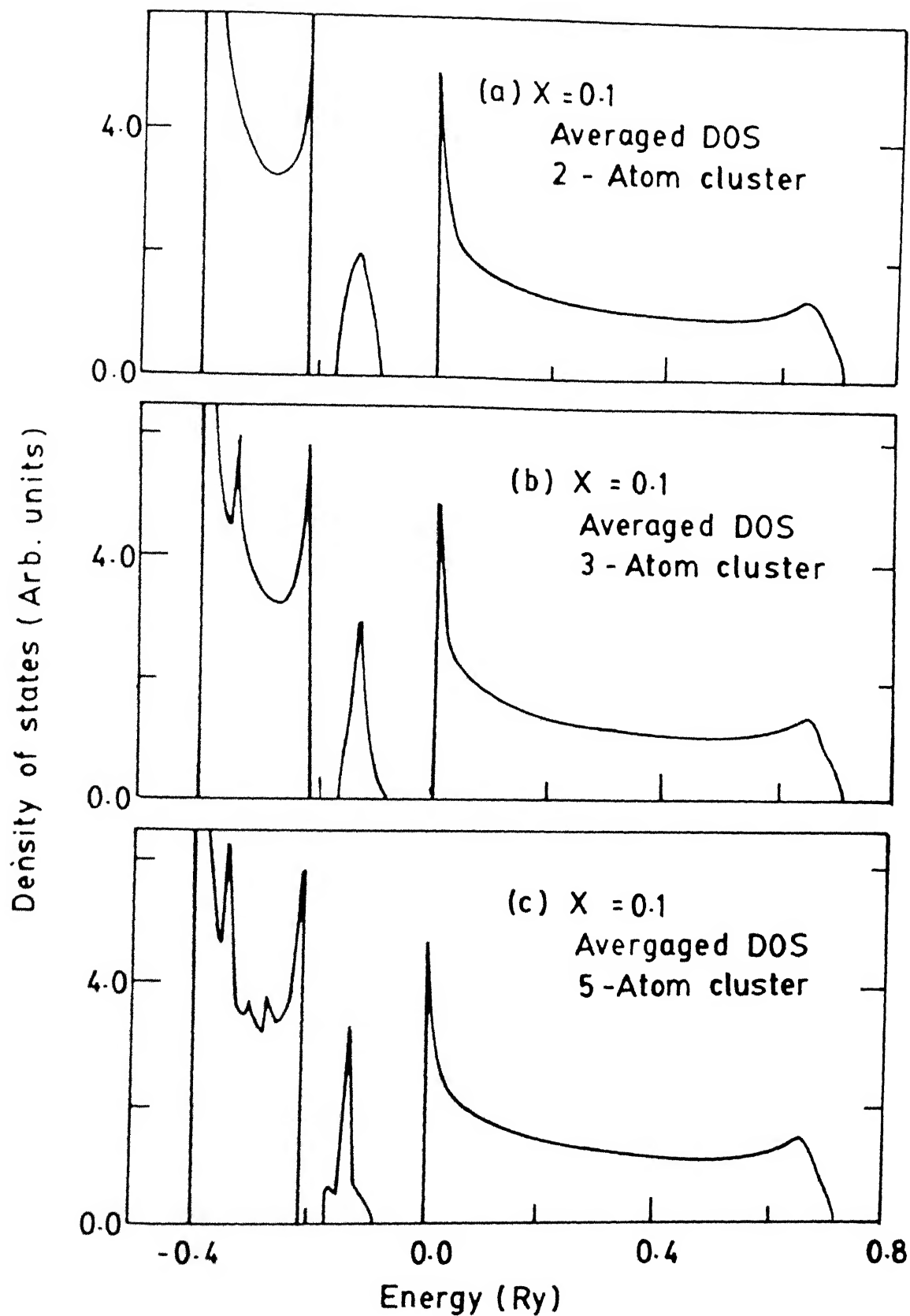
Fig. 4.4 Averaged density of states on the central site of a cluster of (a) two atoms, (b) three atoms, and (c) five atoms, embedded in the KKR-CPA medium for x = 0.1.
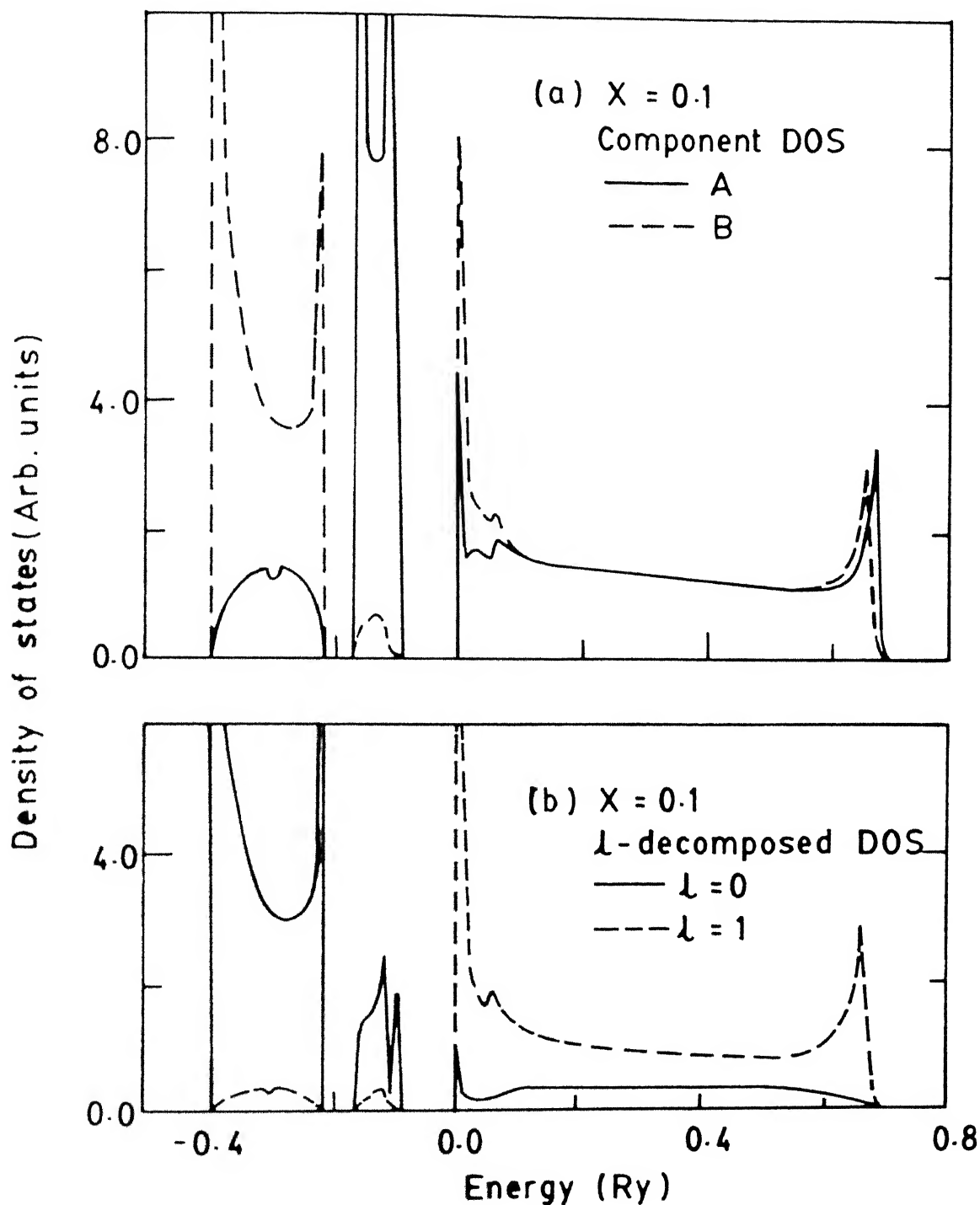
Fig. 4.5 (a) Component density of states on an A-type (solid line) and B-type (dashed line) atom in the alloy with concentration x = 0.1. (b) $l$-decomposed density of states showing $l$ = 0 (solid line) and $l$ =1 (dashed line) components of the averaged density of states for the alloy with concentration x = 0.1.
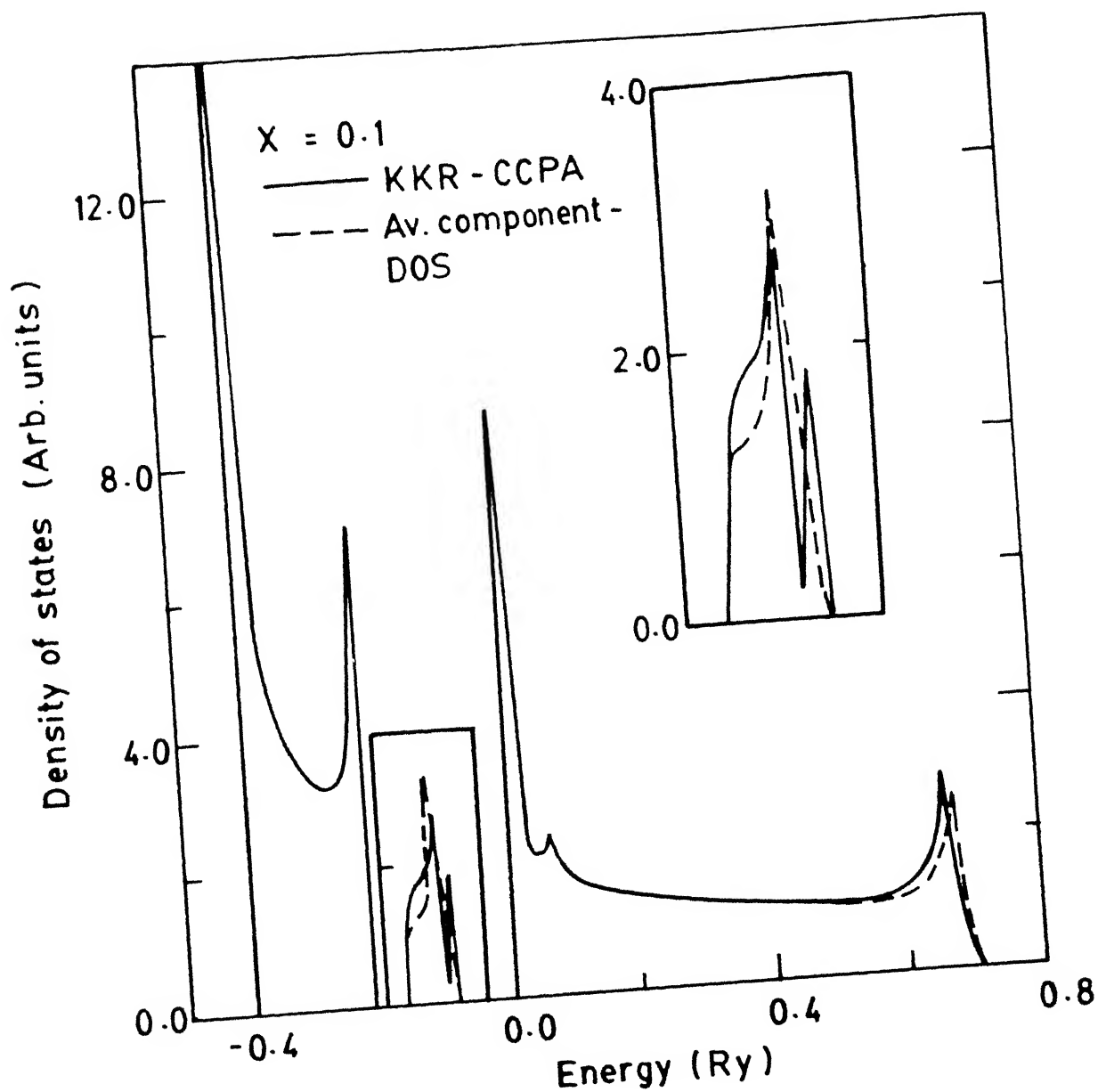
Fig. 4.6 KKR-CCPA density of states (solid line) and the concentration- weighted average of the component density of states (dashed line) for the alloy with concentration x = 0.1. The impurity band is shown in an expanded scale (double) in the inset.

is obtained using the augmented space formalism by exactly averaging over the configurations of a two-atom cluster.

Now we consider the case of a concentrated alloy ($x$ = 0.5). In Fig. 4.7, we show the densities of states calculated within the KKR-CPA and KKR-CCPA. In this case also, we observe that, the KKR-CPA gives a rather smooth density of states besides a peak in each band while the KKR-CCPA, once again gives few extra structures in all the bands. The KKR-CPA peaks at $E = -0.39$ Ry and $E = -0.21$ Ry almost coincide with the major KKR-CCPA peaks at $E = -0.39$ Ry and $E = -0.21$ Ry. Besides these major peaks, we observe some more peaks at $E = -0.35$ Ry, $E = -0.29$, $E = -0.11$ Ry, and $E = -0.05$ Ry, in the KKR-CCPA density of states. As in case of $x=0.1$, these extra structures in the KKR-CCPA density of states, are very close to the structures in the local density of states on the impurities of a two-impurity cluster embedded in the KKR-CPA medium. In Figs. 4.8(a) and 4.8(b), we show respectively the local density of states on the impurities of a cluster of two like and unlike impurities embedded in the KKR-CPA medium. We observe that, the KKR-CCPA peak at $E = -0.35$ Ry is exactly at the position of the peak in the local density of states on a B-type impurity of an AB-type cluster, as shown in Fig. 4.8(b). Thus the KKR-CCPA peak at $E = -0.35$ Ry may be identified as due to the B-type atoms. A small but observable structure at $E = -0.29$
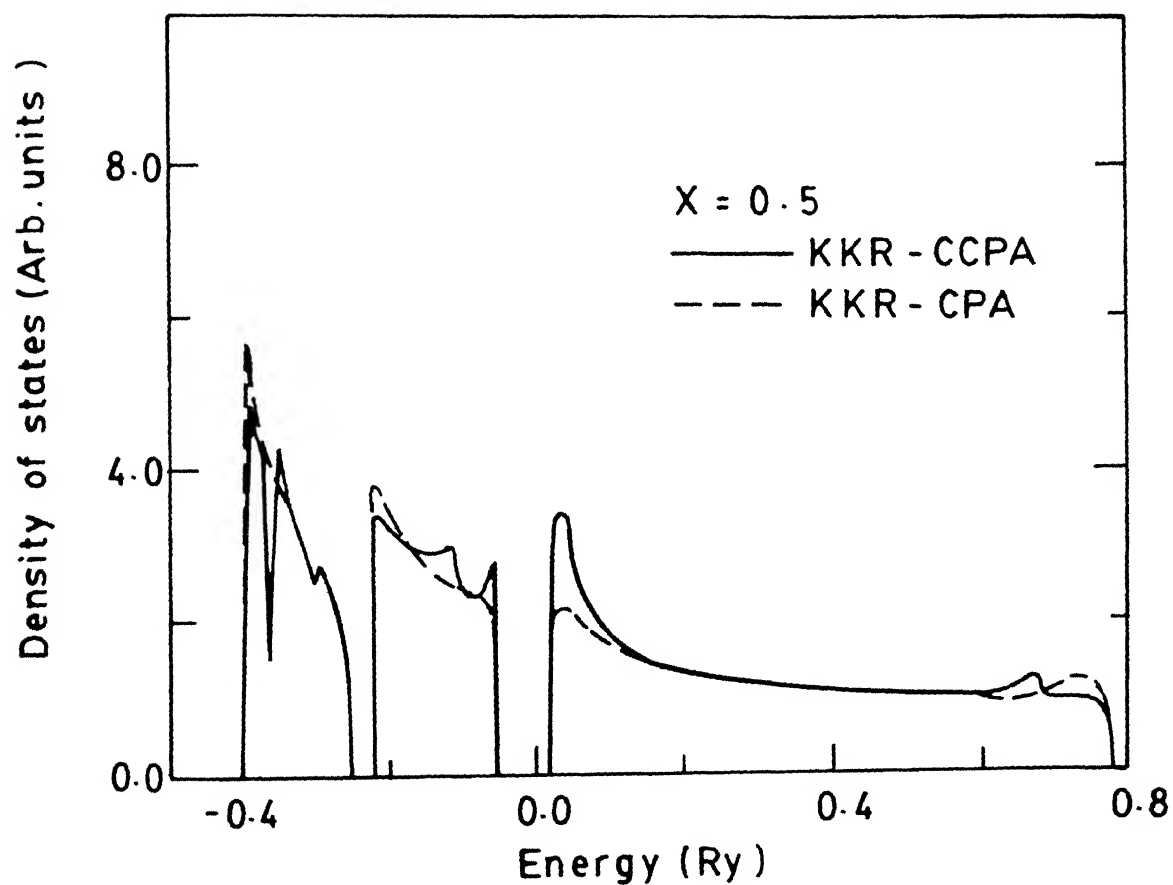
Fig. 4.7 KKR-CPA (dashed line) and KKR-CCPA (solid line) density of states for the alloy with concentration x = 0.5.
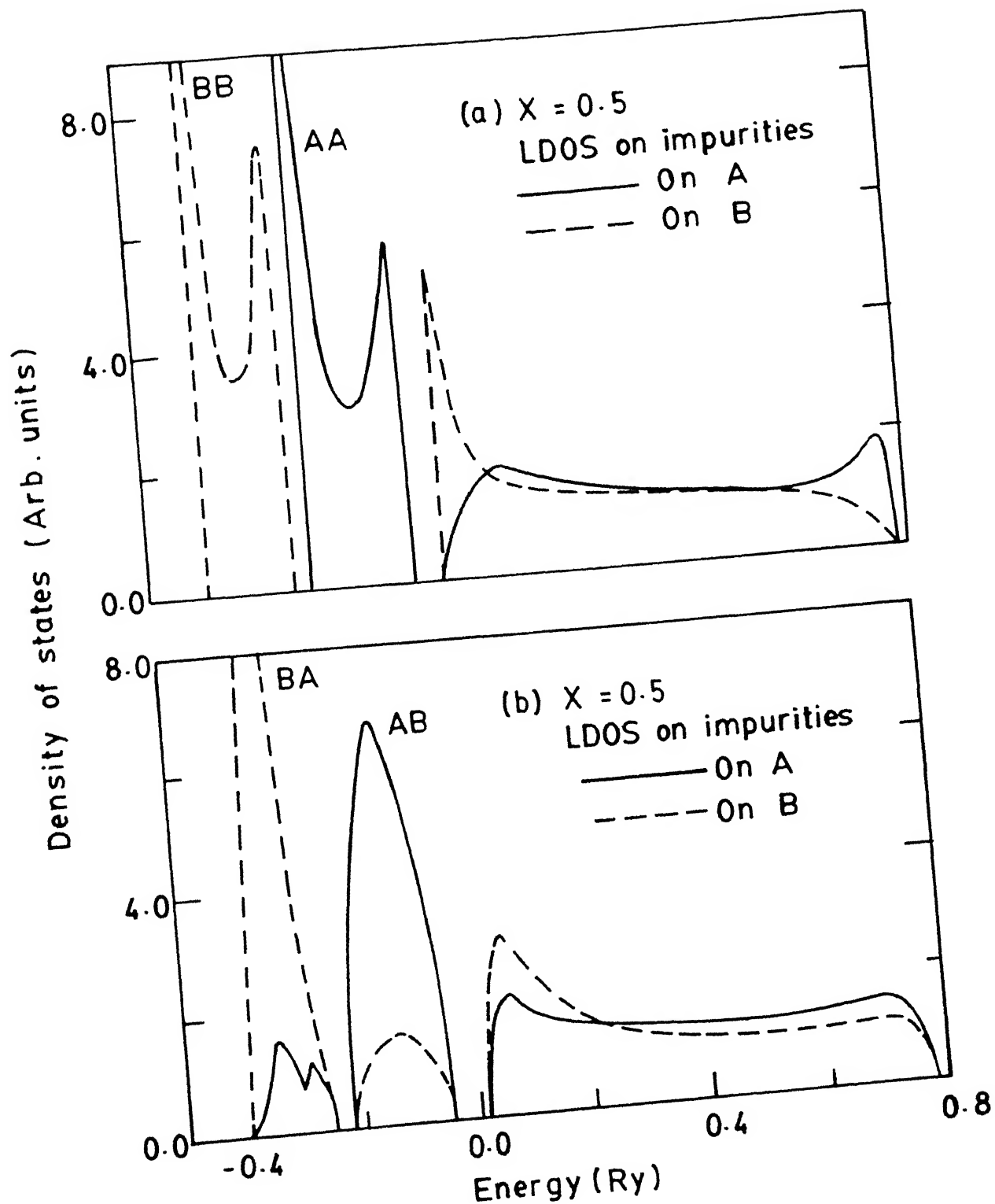
Fig. 4.8 (a) Local density of states on the impurity site for a cluster of two impurities of AA (solid line) and BB (dashed line) type embedded in the KKR-CPA medium for x = 0.5. (b) Local density of states on the impurity site of A (solid line) and B (dashed line) type of an AB-type cluster embedded in the KKR-CPA medium for x = 0.5.

Ry in the KKR-CCPA density of states is at the exact location of a small peak in the local density of states on an A-type impurity of an AB-type cluster (Fig. 4.8(b)). The peak at E = -0.11 Ry is close to the peak in the local density of states on an A-type impurity of an AB-type cluster, which is at E = -0.14 Ry. One more extra peak at E = -0.05 Ry can be identified as due to the A-type atoms as it is exactly at the same location as a peak in the local density of states on an A-type impurity of an AA-type cluster, as shown in Fig. 4.8(a).

In Fig. 4.9, we show the results corresponding to Fig. 4.4, but for a different concentration, x = 0.5. As in the low concentration limit, in this case also, we observe that, the averaged density of states calculated by the embedded cluster method,[60] does reproduce some of the structures of the KKR-CCPA density of states. The structures in the density of states of the embedded cluster method become prominent and sharper, and show an increasing resemblance to the KKR-CCPA density of states with the increase in the cluster-size. The extra structures in the KKR-CCPA density of states at E = -0.35, E = -0.29, and E = -0.11 are reproduced in the density of states of the embedded cluster method, when we take a five-atom cluster. Therefore, we conclude that, the structures in the KKR-CCPA density of
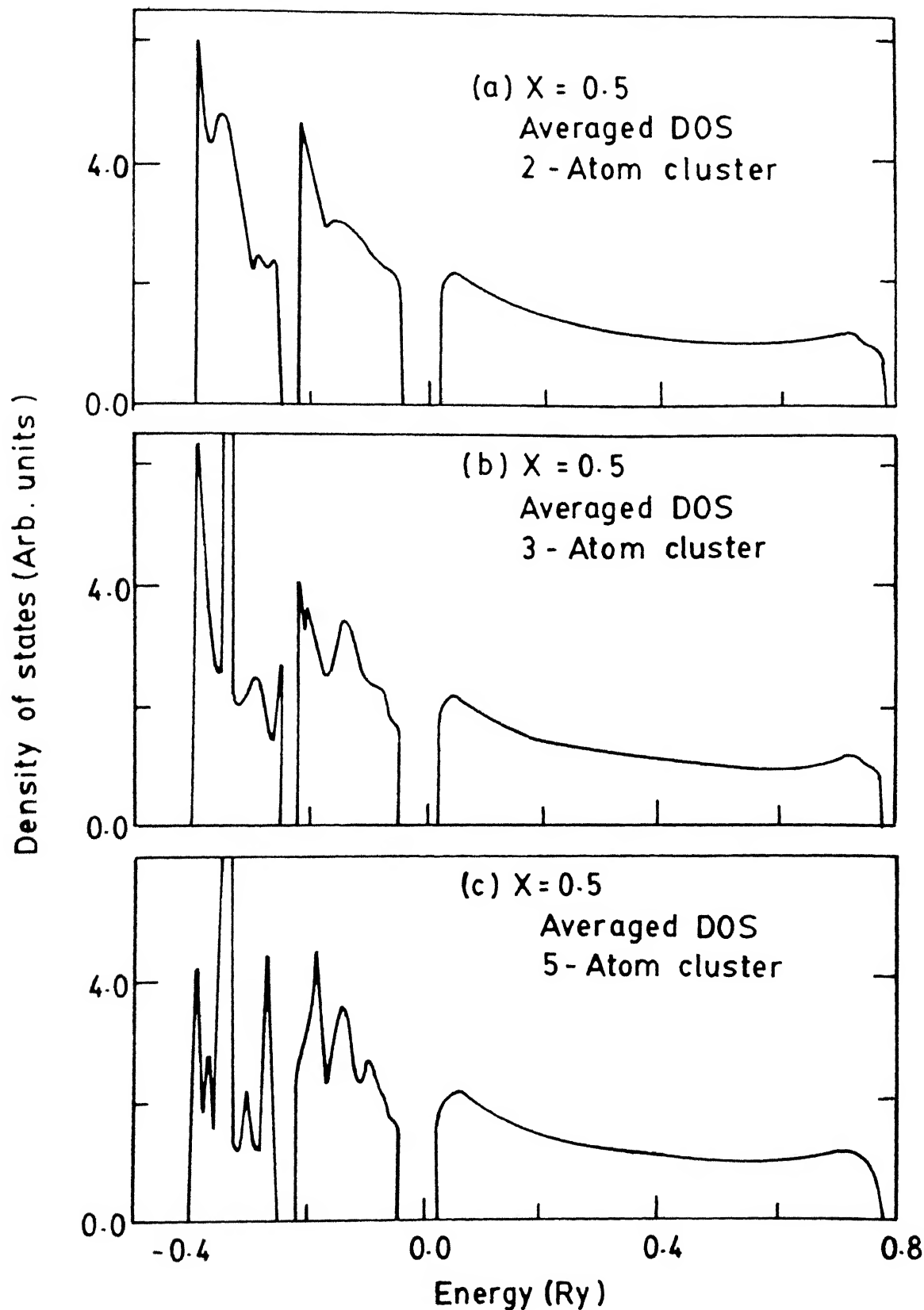
Fig. 4.9 Averaged density of states on the central site of a cluster of (a) two atoms, (b) three atoms, and (c) five atoms, embedded in the KKR-CPA medium for x = 0.5.

states are due to the correlated scattering from clusters of atoms.

In Figs. 4.10(a) and 4.10(b), we show the component density of states and $l$-decomposed KKR-CCPA density of states respectively for x = 0.5. In this case also, we observe that the lowest band is dominantly $l$ = 0 in character.

In Fig. 4.11 we compare the KKR-CCPA density of states and the concentration-weighted average of the component density of states presented in Fig. 4.10(a). Apart from the small structure at E = -0.29 Ry in the KKR-CCPA density of states, both these density of states seem to look alike. But, nevertheless, the height of the peaks are not same in the two cases.

Just to see the effect of the different choices of off-diagonal terms between a real and an effective atom, we have calculated the local density of states on a single impurity embedded in the KKR-CCPA medium using Eq. (4.24), for various impurity potentials with different values of $\mu$. In Fig. 4.12(a), we show the local density of states on A-type impurity (potential-depth = 0.3 Ry) for x=0.1, and $\mu$ = 0.0, 0.5, and 1.0. We observe that, there is some variation in the height of the peaks in the local density of states with $\mu$, although there is little qualitative change in the density of states. The variation in the height of the peaks for $\mu$ = 0.0 and $\mu$ = 1.0 is less than 10%. A similar trend is
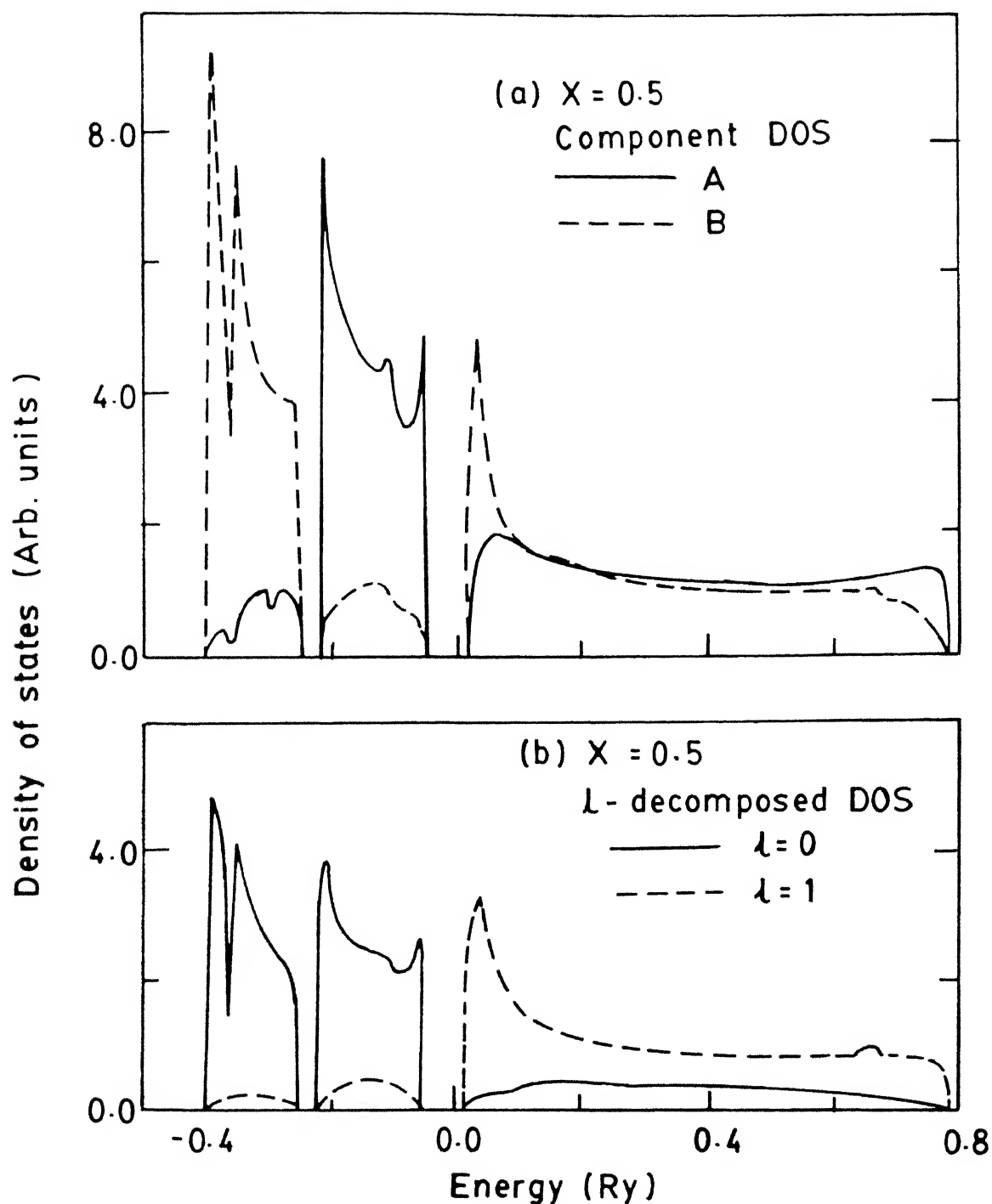
Fig. 4.10 (a) Component density of states on an A-type (solid line) and B-type (dashed line) atom in the alloy with concentration x = 0.5. (b) $\ell$-decomposed density of states showing $\ell$ = 0 (solid line) and $\ell$ =1 (dashed line) components of the averaged density of states for the alloy with concentration x = 0.5.
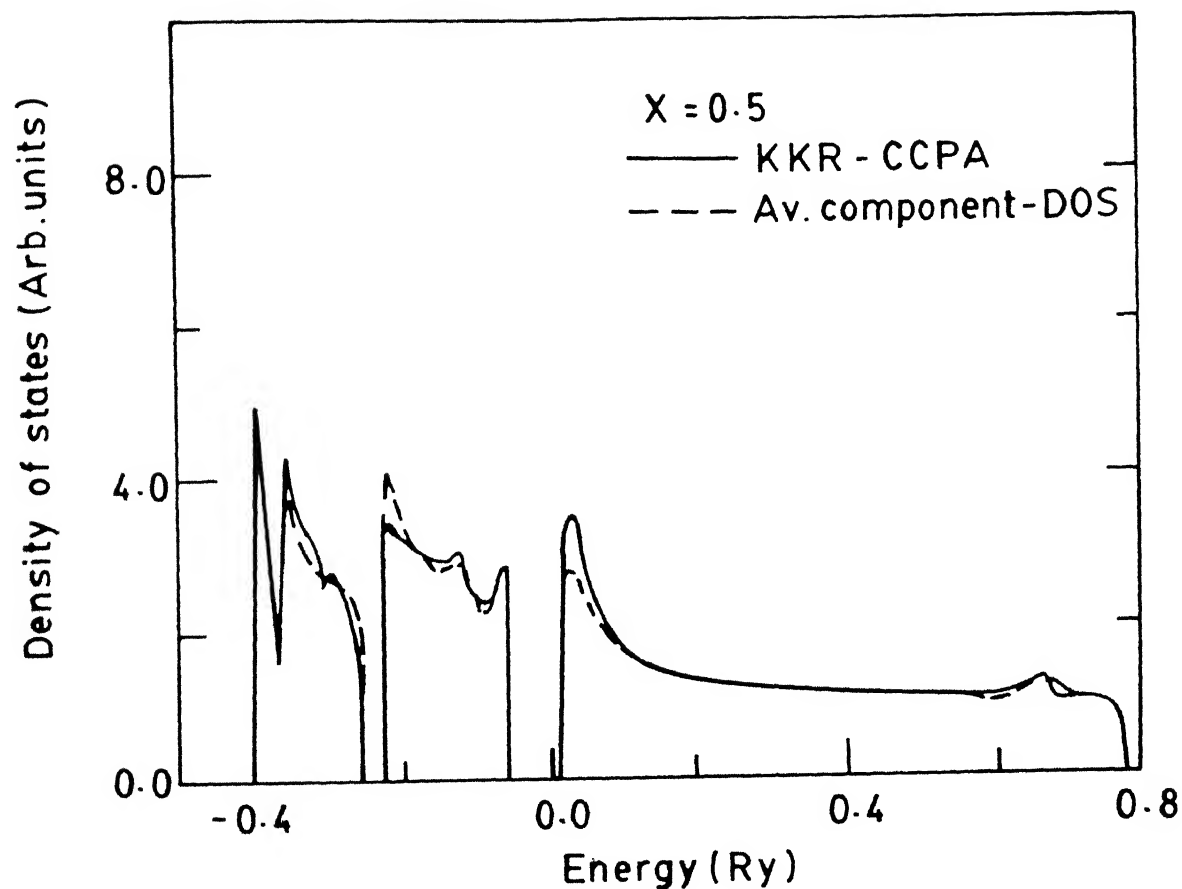
Fig. 4.11 KKR-CCPA density of states (solid line) and the concentration- weighted average of the component density of states (dashed line) for the alloy with concentration x = 0.5.
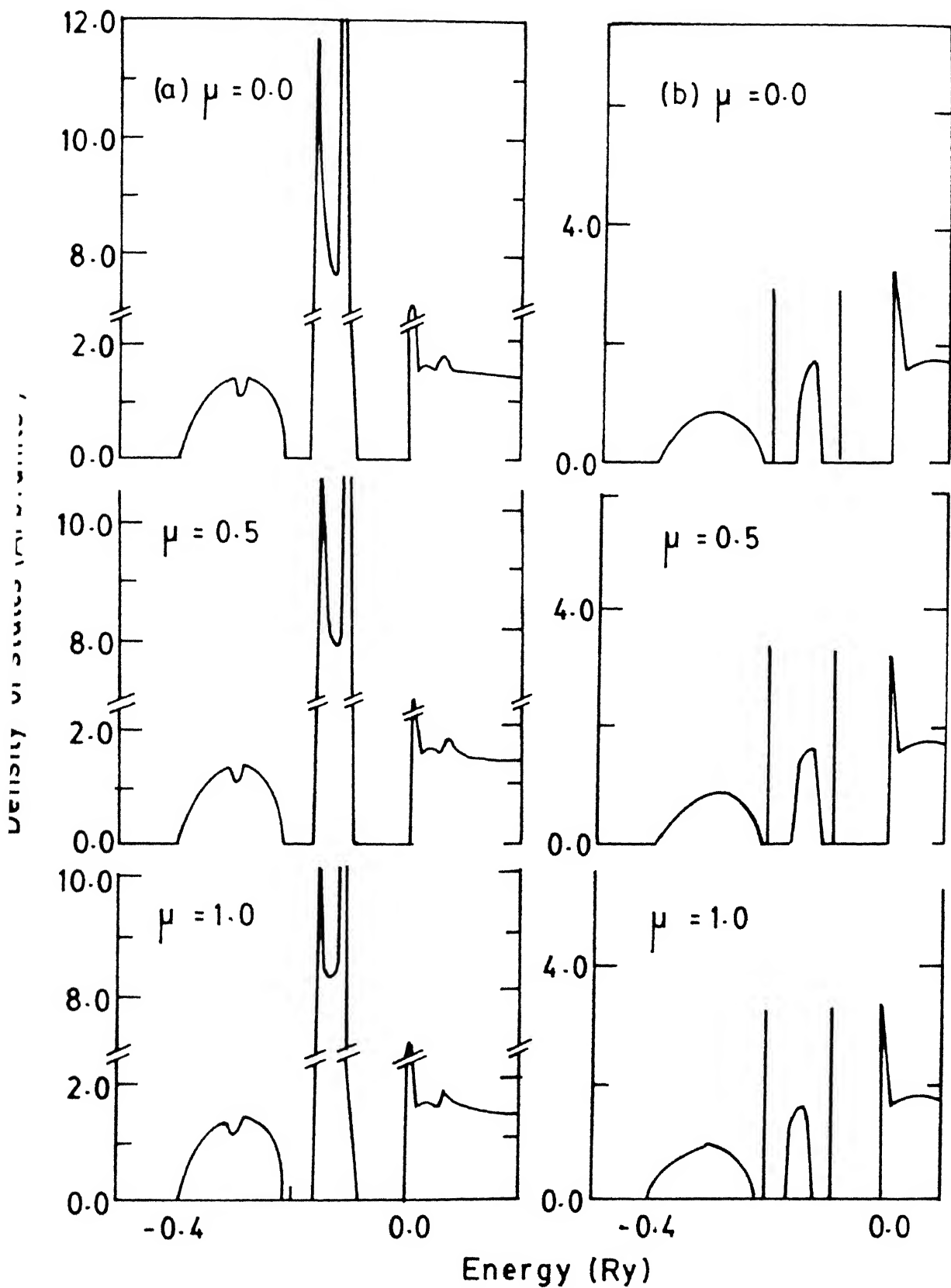
Fig. 4.12 Local density of states on a single impurity of potential-depth (a) 0.3 Ry (type A), and (b) 0.2 Ry, embedded in the KKR-CCPA medium for x = 0.1, using Eq. (4.24) for different values of $\mu$.

observed in the case of x = 0.5. Also, for an impurity of foreign kind, the same conclusion can be drawn from Fig. 4.12(b), which shows local density of states on the impurity of potential-depth 0.2 Ry. It is, therefore, clear that the basic structure of the local density of states does not change with different choices of the off-diagonal terms between real and effective atoms.[67]

## 4.5 CONCLUSIONS

In this chapter, we presented the density of states for a one-dimensional muffin-tin alloy alloy calculated using the KKR-CCPA formulation presented in Chapter 3. We observed that the density of states calculated within the KKR-CCPA is more structured than the KKR-CPA density of states. We were able to correlate these structures with those in the local density of states on the impurities embedded in the KKR-CPA medium. We also found that these structures were missing in the averaged density of states calculated by the embedded cluster method for small clusters. However, when the cluster-size was increased, the embedded cluster method did reproduce some of the structures of the KKR-CCPA density of states. These observations suggest that, the extra

structures in the KKR-CCPA density of states arise due to correlated scattering from clusters of atoms in the effective medium.

Our calculations of the local density of states on a single impurity embedded in the KKR-CCPA medium revealed that the basic structure of the local density of states remains unaltered with different choice of the off-diagonal terms between real and effective atoms.[67] However, we feel that, further work is needed to clarify the problem of embedding in the KKR-CCPA medium.

# CHAPTER 5
# DISORDERED ALLOYS WITH SHORT-RANGE ORDER


## 5.1 INTRODUCTION


The Korringa-Kohn-Rostoker cluster coherent-potential approximation (KKR-CCPA) presented in Chapter 3 is valid for purely random alloys.[67] Many disordered alloys are known to exhibit short-range order.[21,22] By short-range order we mean the tendency of atoms of a given kind to surround atoms of the same kind or of a different kind. The augmented space formalism discussed in Chapter 2, which was used to develop the KKR-CCPA formulation, has the restriction that, the site occupation variables $\{n_i\}$ be statistically independent.[52,54] In other words, the probability of a particular kind of atom occupying a given site was assumed to be completely independent of the surrounding environment. However, for disordered systems with short-range order, this assumption is not valid. Disordered systems with short-range order can only be described in terms of dependent random variables. Thus, the augmented space formalism, presented in Chapter 2, can not be applied to these systems. However, the augmented space formalism can be generalized so that functions of dependent random variables can also be averaged.[70,94,95]

This new formalism has already been applied to disordered alloys in the tight-binding framework.[70] Our aim in this chapter is to extend this technique to the KKR-CCPA formulation presented in Chapter 3.

We have applied the generalized augmented space formalism to obtain an expression for the configuration averaged Green's function[96] for systems with short-range order. This averaged Green's function is exact, and therefore, analytic. This is essentially an expansion of the configuration averaged Green's function in presence of short-range order about that for a random system, and contains an infinite series.[70,96] For numerical computations, we need to truncate this series after a few manageable terms. In the present work, we truncate the series after the first correction term. Using this formulation, we have calculated the density of states for the one-dimensional muffin-tin alloy with Markovian type short-range order.[70] We find that, our approximation yields non-negative density of states at all energies for a reasonably wide range of short-range order parameter. However, when the short-range order is strong, the density of states becomes negative in certain energy regions. This may be due to the approximation, in which we neglected the higher order correction terms in the expansion of the configuration

averaged Green's function. The higher order terms may be important in the strong short-range order regime. We have compared our results with those obtained by the embedded cluster method of Gonis and Freeman.[50] We find that there is a general agreement between the two results.

In section 5.2, we outline some mathematical preliminaries which we will need in the development of the theory. In section 5.3, we derive an expression for the configuration averaged Green's function for disordered alloys with short-range order. In section 5.4, we describe the Markov chain[70,73] and we present our results in section 5.5. Finally, in section 5.6, we outline the limitations and shortcomings of the theory.

## 5.2 MATHEMATICAL PRELIMINARIES

In Chapter 2, we mentioned that, a particular configuration of a disordered alloy can be described in terms of a set of occupation variables $\{n_i\}$, in a particular sequence, and that a certain probability density $\mathcal{P}(\{n_i\})$ is associated with each of these configurations. The simplest case that represents a disordered alloy is one in which $\{n_i\}$ are independent random variables. For this case, it is

possible to decompose $\mathcal{P}(\{n_i\})$ as a product of individual probability densities of all the sites,[52] i.e.

$$\mathcal{P}_{random}(\{n_i\}) = \prod_i p_i(n_i). \tag{5.1}$$

However, when $\{n_i\}$ are not statistically independent, such a decomposition is not possible. But, nevertheless, it is possible to decompose $\mathcal{P}(\{n_i\})$ into two parts such that, the short-range order part is separated.[70] In the following we give the mathematical justification of the above statement.

The probability density, $\mathcal{P}(\{n_i\})\prod_i dn_i$ of a particular configuration is a 'measure' of how probable that particular configuration is, i.e.

$$d\mu = \mathcal{P}(\{n_i\}) \prod_i dn_i , \tag{5.2}$$

where $\mu$ is the measure.[97] It is evident that, the measure will be different depending on whether $\{n_i\}$ are independent or dependent random variables. We define

$$d\mu_1 = \mathcal{P}_{random}(\{n_i\})\prod_i dn_i , \tag{5.3}$$

and

$$d\mu_2 = \mathcal{P}_{SRO}(\{n_i\}) \prod_i dn_i , \tag{5.4}$$

where $\mathcal{P}_{SRO}(\{n_i\})$ is the probability density in presence of short-range order. We note that, in a random distribution, all the configurations are 'probable', however, in presence of short-range order, some or other configurations may be missing. In other words, if a configuration is allowed in the presence of short-range order, it must be present in a random distribution.[70] In a random distribution, the only configurations missing are those which are not consistent with the concentrations of the constituent atoms. Obviously, these configurations must be absent in presence of short-range order as well. In terms of measure, it can be stated as, if $\mu_1 = 0$, then $\mu_2 = 0$. However, the reverse is not true. In measure theory,[97] this condition is stated as, $\mu_2$ is 'absolutely continuous' with respect to $\mu_1$. A basic theorem about the absolute continuous measures in measure theory is the Radon-Nikodym theorem.[97] When we apply this theorem to the present problem, it implies that it is possible to write,[70]

$$d\mu_2 = \phi(\{n_i\}) \, d\mu_1 \qquad (5.5)$$

where $\phi(\{n_i\})$ is called the Radon-Nikodym derivative of $\mu_2$ with respect to $\mu_1$. Therefore, we may write,[70]

$$\mathcal{P}_{SRO}(\{n_i\}) = \Phi(\{n_i\})\, \mathcal{P}_{random}(\{n_i\}) = \Phi(\{n_i\}) \prod_i p_i(n_i).$$

$$(5.6)$$

The advantage of Eq. (5.6) is that, it allows one to calculate configuration averaged properties of a system with short-range order in terms of averages which are computed with respect to independent random variables.[70] The price one pays for this simplification, is the introduction of an unknown function $\Phi(\{n_i\})$. However, we will show that, it does not present any difficulty.

## 5.3 THE CONFIGURATION AVERAGED GREEN'S FUNCTION

We consider a general function $E(\{n_i\})$ of dependent random variables (i.e. with short-range order). The configuration average of $E(\{n_i\})$ is given by,

$$\left[\langle E \rangle\right]_{SRO} = \int E(\{n_i\})\, \mathcal{P}_{SRO}(\{n_i\}) \prod_i dn_i .$$

$$(5.7)$$

For the configuration average of a function for a random system we will use the notation $\langle E \rangle$, which we have been using so far.

Substituting Eq. (5.6) in Eq. (5.7), we get,

$$\left[\langle E \rangle\right]_{SRO} = \int E(\{n_i\})\, \Phi(\{n_i\}) \prod_i p_i(n_i) dn_i .$$

$$(5.8)$$

Now we are in a position to apply the augmented space theorem[52] given by Eq. (2.19) to Eq. (5.8), which gives us,

$$\left[\langle E \rangle\right]_{SRO} = \langle f | \ \tilde{E}(\{M^i\}) \ \tilde{\phi}(\{M^i\}) \ | f \rangle, \qquad (5.9)$$

where $\tilde{E}(\{M^i\})$ and $\tilde{\phi}(\{M^i\})$ are obtained by replacing $\{n_i\}$ in $E(\{n_i\})$ and $\phi(\{n_i\})$ by $\{M^i\}$. In order to use Eq. (5.9), we need to know $\tilde{\phi}(\{M^i\}) | f \rangle$. We note that, $\tilde{\phi}(\{M^i\})$ is a function of $\{M^i\}$ only, and therefore, is an operator in the configuration space alone (i.e. it is independent of the real Hilbert space). Thus, we can expand $\tilde{\phi}(\{M^i\}) | f \rangle$ in terms of the complete set of basis vectors in the configuration space,[70] i.e.

$$\tilde{\phi}(\{M^i\}) | f \rangle = \sum_{\sigma} a_{\sigma} \ | f_{\sigma} \rangle, \qquad (5.10)$$

where

$$a_{\sigma} = \langle f_{\sigma} | \ \tilde{\phi}(\{M^i\}) | f \rangle. \qquad (5.11)$$

Substituting Eq. (5.10) in Eq. (5.9) we get,

$$\left[\langle E \rangle\right]_{SRO} = \sum_{\sigma} a_{\sigma} \ \langle f | \tilde{E}(\{M^i\}) | f_{\sigma} \rangle \equiv \sum_{\sigma} a_{\sigma} \left[\tilde{E}(\{M^i\})\right]^{0\sigma}. \qquad (5.12)$$

The coefficients $a_\alpha$ can be easily determined from known joint distribution functions. Putting $E(\{n_i\}) = 1$, in Eq. (5.12), we immediately get

$$a_\emptyset = 1. \qquad (5.13)$$

Putting $E(\{n_i\}) = n_i$, in Eq. (5.12) we get

$$\langle n_i \rangle = \sum_\alpha a_\alpha \langle f| \; M^i \; |f_\alpha \rangle. \qquad (5.14)$$

Using Eq. (3.44a), we immediately get

$$\langle n_i \rangle = x \; a_\emptyset + (xy)^{1/2} \; a_i \; ,$$

which readily gives us,

$$a_i = 0, \; \text{for all } i, \qquad (5.15)$$

because, $\langle n_i \rangle = x$. Similarly, if we put $E(\{n_i\}) = n_i n_j$ in Eq. (5.12), we get

$$\langle n_i n_j \rangle = \sum_\alpha a_\alpha \langle f| \; M^i \; M^j |f_\alpha \rangle,$$

which with the help of Eqs. (3.44a) and (3.44c), gives us,

$$\langle n_i n_j \rangle = a_0 \, x^2 + x \, (xy)^{1/2} \, ( a_i + a_j) + xy \, a_{ij} \, . \qquad (5.16)$$

With the help of Eqs. (5.13) and (5.15) we get,

$$a_{ij} = [ \ \langle n_i n_j \rangle - x^2 \ ]/xy. \qquad (5.17)$$

From the definition of $\{n_i\}$ (Eq. (2.32)), we get

$$\langle n_i n_j \rangle = P_{AA}^{ij} \, , \qquad (5.18)$$

i.e. it is the probability of having A-type atoms on i-th and j-th sites. In a random distribution $P_{AA}^{ij} = x^2$, so that $a_{ij}$ vanishes in this case. In the present case, we have

$$a_{ij} = [ \ P_{AA}^{ij} - x^2 \ ]/xy. \qquad (5.19)$$

In a similar manner, we can evaluate all the coefficients.[70] In the following we list a few of them.

$$a_{ijk} = [ P_{AAA}^{ijk} - x (P_{AA}^{ij} + P_{AA}^{jk} + P_{AA}^{ki}) - 2x^3 ]/(xy)^{3/2} \qquad (5.20)$$

$$a_{ijkl} = [ P_{AAAA}^{ijkl} - x (P_{AAA}^{ijk} + P_{AAA}^{jkl} + P_{AAA}^{kli} + P_{AAA}^{lij}) + x^2 (P_{AA}^{ij} +$$

$$P_{AA}^{jk} + P_{AA}^{kl} + P_{AA}^{li} + P_{AA}^{ik} + P_{AA}^{jl}) - 3x^4 ]/(xy)^2 \qquad (5.21)$$

and so on.

The configuration averaged Green's function can be written from Eq. (5.12) as,

$$\left[ \langle G \rangle \right]_{SRO} = \sum_{\sigma} a_{\sigma} \, \langle f | \tilde{G}(\{M^i\}) | f_{\sigma} \rangle. \qquad (5.22)$$

This is an infinite sum. The first term in the series, which is $\langle f | \tilde{G}(\{M^i\}) | f \rangle$, is the configuration averaged Green's function for a purely random system. Therefore, Eq. (5.22) can be regarded as a perturbation expansion, when the higher terms in the series come as a perturbation to the averaged Green's function of the random distribution. Thus, Eq. (5.22) allows us to calculate the averaged Green's function in presence of short-range order, in terms of the random averages.[70]

If we apply this technique to the site-diagonal form of the KKR Green's function, we will very easily get,

$$\left[ \langle G_{SD} \rangle \right]_{SRO} = \langle G_{SD} \rangle + \text{Tr} \sum_{\sigma \neq 0} a_{\sigma} \left[ \langle 0;f | \left[ \tilde{A}(\{M^i\}) \right]^{-1} | 0;f_{\sigma} \rangle \, F^B + \right.$$

$$\left. \langle 0;f | \left[ \tilde{A}(\{M^i\}) \right]^{-1} M^o | 0;f_{\sigma} \rangle \, \delta F \right], \qquad (5.23)$$

where $\langle G_{SD} \rangle$ is given by Eq. (3.116). Since Eq. (5.23) involves an infinite sum, it can not be used for numerical computations. Therefore, we have to introduce some

approximation, i.e. to terminate the sum after a few steps. In our calculation, we have terminated the sum after two steps. In this case, only $a_{ij}$ are non-zero (because, all $a_i$'s are zero, Eq. (5.15)). When we apply the CCPA to the present case, the number of terms to be summed can be further reduced. For a two-atom cluster consisting of sites 0 and 1, the only non-zero term in the expansion corresponds to $a_{01}$. This essentially means that, we keep only the first correction term in the expansion of the configuration averaged Green's function about the averaged Green's function of the random system. With this approximation, Eq. (5.23) can be written as

$$\left[\langle G_{SD}\rangle\right]_{SRO} = \langle G_{SD}\rangle + \frac{1}{xy}\left[P_{AA}^{01} - x^2\right] \text{Tr}\left[\langle 0;f|\tilde{A}^{-1}|0;f_{01}\rangle F^B + \langle 0;f|\tilde{A}^{-1}M^o|0;f_{01}\rangle \delta F\right].$$

(5.24)

Using Eq. (3.44d), we get

$$\left[\langle G_{SD}\rangle\right]_{SRO} = \langle G_{SD}\rangle + \frac{1}{xy}\left[P_{AA}^{01} - x^2\right] \text{Tr}\left[\langle 0;f|\tilde{A}^{-1}|0;f_{01}\rangle \tilde{F} + \langle 0;f|\tilde{A}^{-1}|0;f_1\rangle \delta F\right],$$

(5.25)

where

$$\tilde{F} = y\,F^A + x\,F^B.$$

The matrix elements of $\tilde{A}^{-1}$ appearing in Eq. (5.25) can be calculated easily,

$$\langle 0;f|\tilde{A}^{-1}|0;f_{01}\rangle = (C_{eff} - \mathcal{X}_2^{00})\,\omega\,Q^{00} - (v^{01} + b^{01})\,\omega\,Q^{01},$$

(5.26)

and

$$\langle 0;f|\tilde{A}^{-1}|0;f_1\rangle = (C_{eff} - \mathcal{X}_2^{00})\,\omega\,\langle 0;f_{01}|\mathcal{A}_2^{-1}|0;f_1\rangle -$$

$$(v^{01} + b^{01})\,\omega\,b^{10}.$$

(5.27)

The variables appearing in Eqs. (5.26) and (5.27) are defined in Chapter 4 (section 4.3). Therefore, the only unknown quantity in Eq. (5.25) is $P_{AA}^{01}$, which we will define in the next section.

## 5.4 MARKOV CHAIN

This is the simplest possible system, for which short-range order can be easily defined. The name comes from a well-known process in the probability theory, called Markov process.[98] In a Markov process, the probability of the i-th event is restricted to depend only on the probability of the (i-1)-th event. By a close analogy, in a Markov chain,[70] the occupation probability of i-th site is assumed to depend only

on the kind of atom occupying its first nearest-neighbor sites. Therefore, in a Markov chain, the short-range order is restricted to nearest-neighbor pairs only. Following Kumar $et$ $al$,[46] we define the nearest-neighbor pair distribution as:

$$p(n_j , n_i = 1) = (1- \alpha y) \delta(n_j - 1) + \alpha y \delta(n_j), \qquad (5.28)$$

and

$$p(n_j , n_i = 0) = \alpha x \delta(n_j - 1) + (1- \alpha x) \delta(n_j). \qquad (5.29)$$

Here $\alpha$ is the parameter that describes the short-range order. It is easily seen that, $\alpha = 1$ represents a system with no short-range order, for $\alpha < 1$, AA- and BB-type clustering is favored, and for $\alpha > 1$, AB-type ordering would be dominant. The maximum value $\alpha = 1/y$ corresponds to a situation, when the alloy is not random at all, but forms a superlattice of A and B constituents. The minimum value $\alpha = 0$ corresponds to a situation, when A- and B-type atoms are totally segregated. When $\alpha$ is close to unity, the short-range order is weak.

From Eq. (5.28), we easily get

$$p_{AA}^{01} = x (1 - \alpha y) = xy (1 - \alpha) + x^2. \qquad (5.30)$$

We will use this form of $P_{AA}^{01}$ in Eq. (5.25), for the calculation of the density of states of this system.

## 5.5 RESULTS AND DISCUSSION

We have calculated the density of states for the one-dimensional muffin-tin alloy with Markovian type short-range order. In Fig. 5.1 and 5.2, we present the results for x = 0.1 for various values of short-range order parameter $\alpha$. Fig. 5.1(a) shows the density of states for $\alpha$ = 1.0, which corresponds to the random alloy. In Fig. 5.1(b), we show the density of states for $\alpha$ = 1.11, which is the maximum allowed value of $\alpha$ for x = 0.1. We observe that, there is little difference between this density of states and the density of states for a random system. In Figs. 5.2(a) and 5.2(b), we show the density of states for $\alpha$ = 0.5, $\alpha$ = 0.75, and $\alpha$ = 0.25 respectively. We note that, for $\alpha$ = 0.25, the density of states becomes negative in the region between E = -0.17 Ry and E = -0.09 Ry. The range of $\alpha$, for which the density of states is non-negative throughout the whole energy range is from 0.25 to 1.11, which is appreciable. We observe a general trend in these results. We note that, when $\alpha$ decreases gradually, some states are pushed into the first majority band, while the impurity band goes on decreasing

Fig. 5.1 Averaged density of states for the alloy with short-range order, for the concentration x = 0.1. The short-range order parameters are (a) α = 1.0 and (b) α = 1.11.
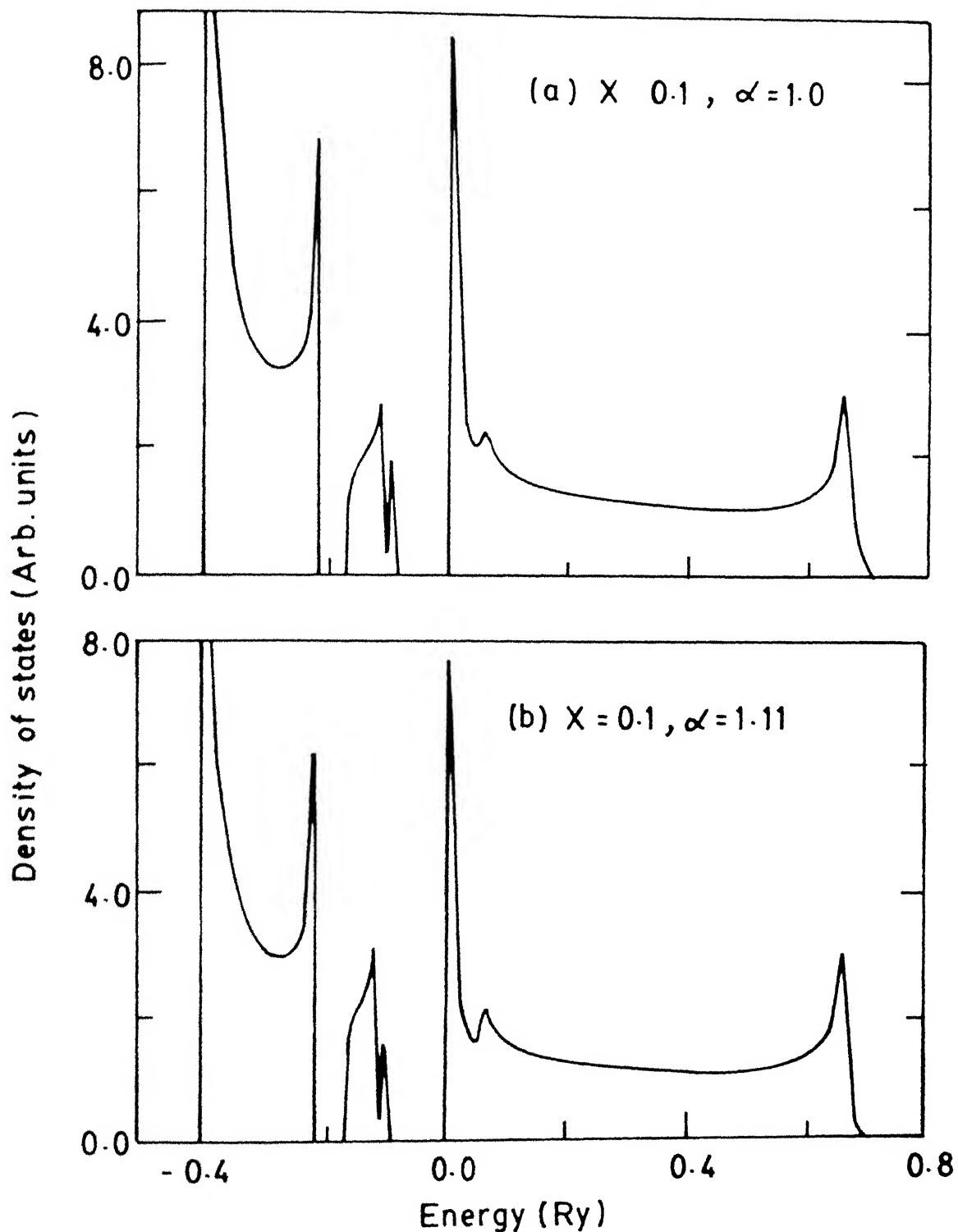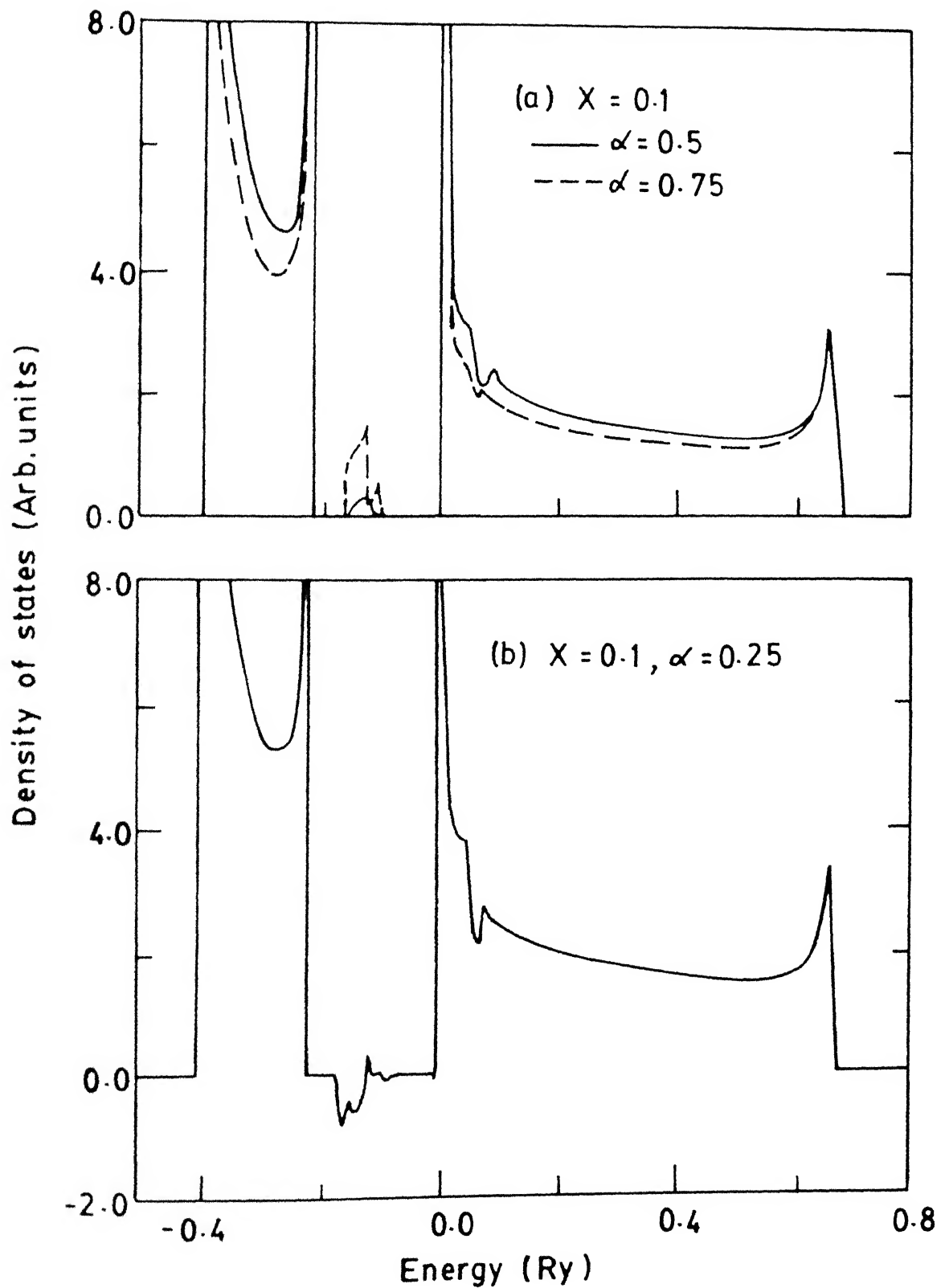
Fig. 5.2 Averaged density of states for the alloy with short-range order, for the concentration x = 0.1. The short-range order parameters are (a) $\alpha$ = 0.75 (dashed line), $\alpha$ = 0.50 (solid line), and (b) $\alpha$ = 0.25.

with $\alpha$. This is because, when $\alpha$ decreases, the probabilities of BB and AA pairs increases, while that of an AB pair decreases. For $x = 0.1$, the probability of a BB pair is quite large compared to the other clusters. Hence, with the decrease in $\alpha$, the system tends towards a pure B system. Therefore, the impurity band, which is the characteristics of A-type atoms, decreases gradually with the decrease in $\alpha$. We have compared our results with those calculated by the embedded cluster method of Gonis and Freeman,[50] in which one can include the effects of short-range order, but in a non-self-consistent way. In Figs. 5.3 and 5.4, we show the density of states obtained by this method, for various values of $\alpha$. In this case also, we observe that, with the decrease in $\alpha$, the impurity band loses some states, while the first majority band gains. Thus, there is a general agreement between the two results.

In Figs. 5.5 and 5.6, we show the density of states calculated by our formulation for $x = 0.5$. In Figs. 5.5(a), 5.5(b), and 5.5(c), we show the density of states for $\alpha = 1.0$ (random), $\alpha = 1.25$, and $\alpha = 1.5$ respectively. In this case also, we observe that, when $\alpha = 1.5$, which is much away from the value corresponding to the random distribution ($\alpha = 1.0$), the density of states becomes negative in some energy regions. In Figs. 5.6(a) and 5.6(b), we show the results for $\alpha = 0.5$, $\alpha = 0.75$, and $\alpha = 0.25$ respectively. Again, we
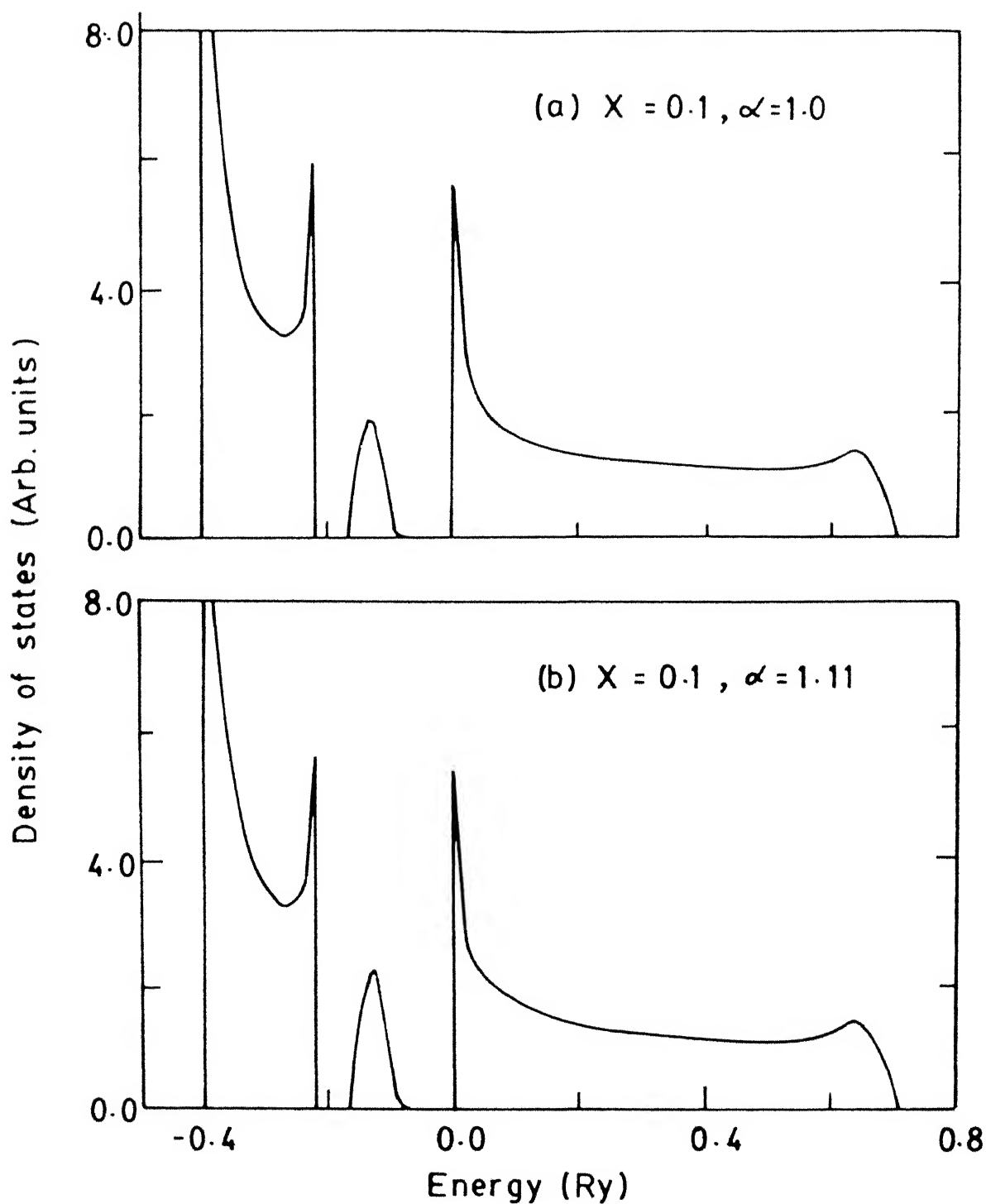
Fig. 5.3 Averaged density of states for the alloy with short-range order, for the concentration x = 0.1 by the embedded cluster method of Ref. 50. The short-range order parameters are (a) $\alpha$ = 1.0 and (b) $\alpha$ = 1.11.
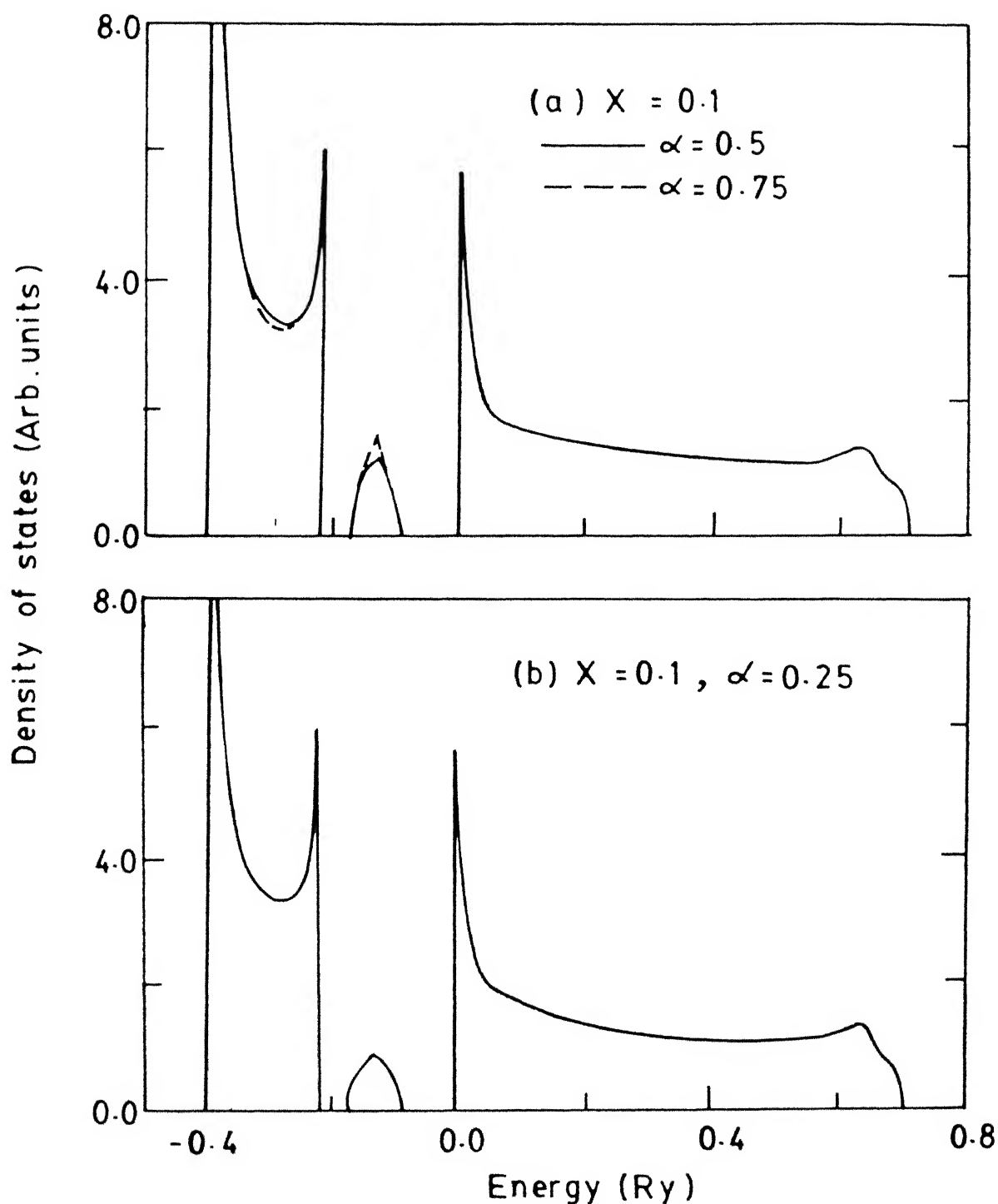
Fig. 5.4 Averaged density of states for the alloy with short-range order, for the concentration x = 0.1 by the embedded cluster method of Ref. 50. The short-range order parameters are (a) α = 0.75 (dashed line), α = 0.50 (solid line), and (b) α = 0.25.
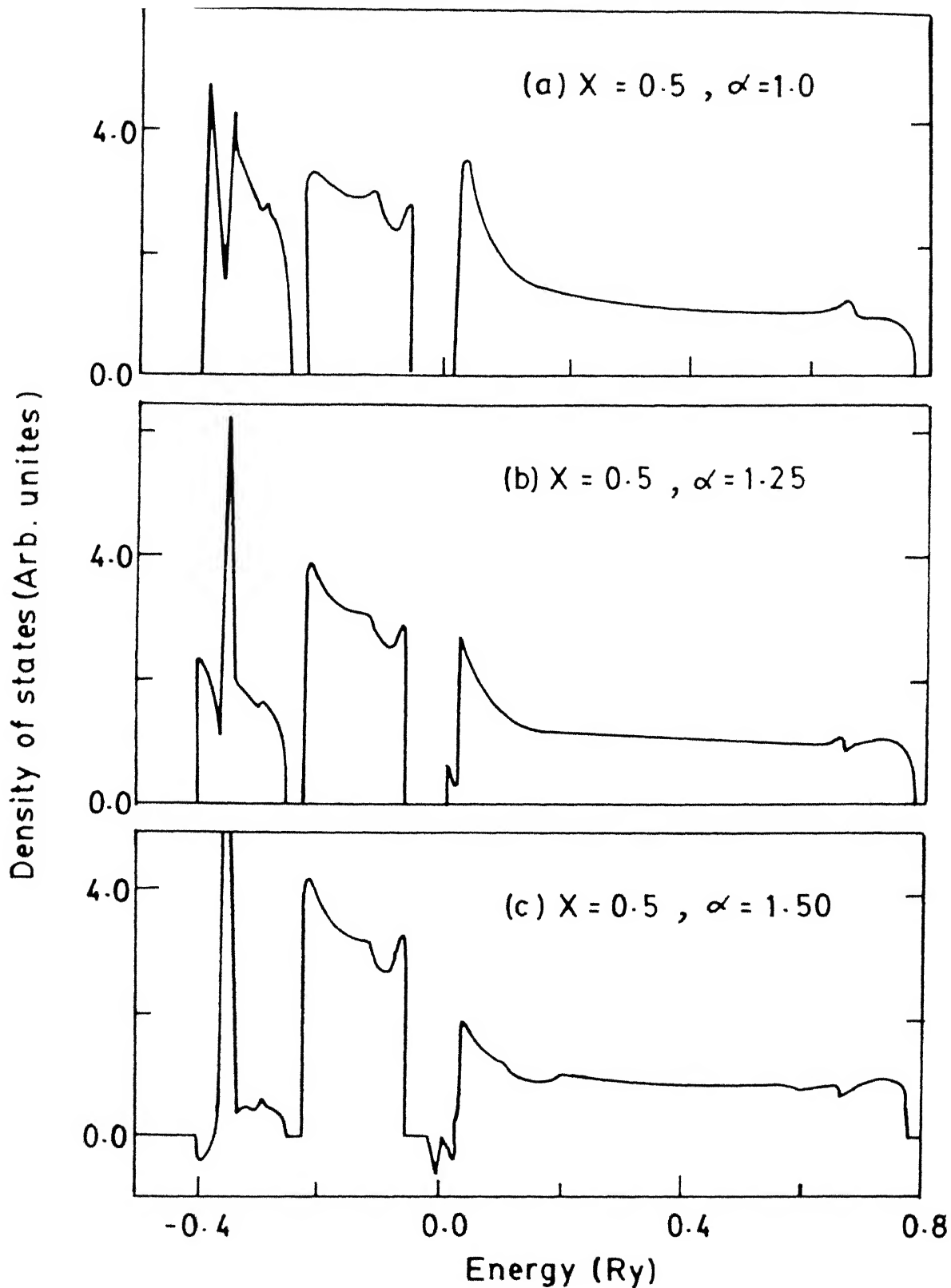
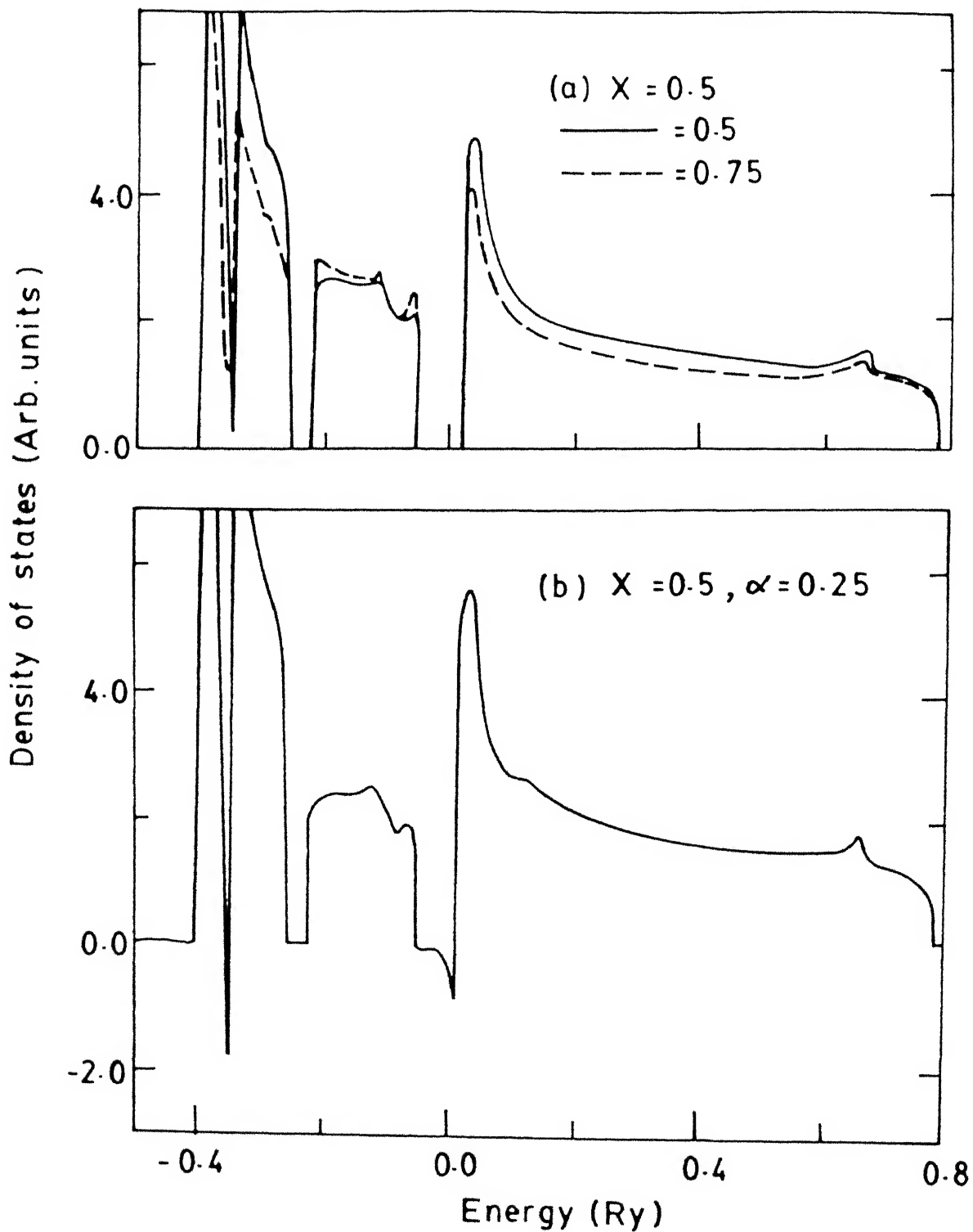Fig. 5.5 Averaged density of states for the alloy with short-range order, for the concentration x = 0.5. The short-range order parameters are (a) α = 1.0, (b) α = 1.25, and (c) α = 1.50.

Fig. 5.6 Averaged density of states for the alloy with short-range order, for the concentration x = 0.5. The short-range order parameters are (a) α = 0.75 (dashed line), α = 0.50 (solid line), and (b) α = 0.25.

observe that, for $\alpha = 0.25$, the density of states becomes negative in some energy regions. In this case also, the range of $\alpha$, for which we get non-negative density of states is appreciable (from 0.25 to 1.50). We find that, as $\alpha$ decreases, states are pushed into the first band. This is expected, since the first band is the characteristics of B-type atoms, and with the decrease in $\alpha$, the probability of BB pairs increases. In Figs. 5.7 and 5.8, we show the corresponding results calculated by the embedded cluster method. We note that, there is a general agreement between these results and the results obtained by our formulation.

It is clear from the above discussion that the approximation in which we have neglected the higher order correction terms in the expansion of the configuration averaged Green's function, gives non-negative density of states for a considerably wide range of the short-range order parameter $\alpha$. It gives negative density of states only when $\alpha$ is very far from unity, when the higher order terms in the expansion become important. It may be mentioned that, one-dimensional systems are known to be very sensitive to approximations. The fact that, our approximation is reasonably good for a one-dimensional system, gives one hope that, it will be quite satisfactory when applied to a three-dimensional system.

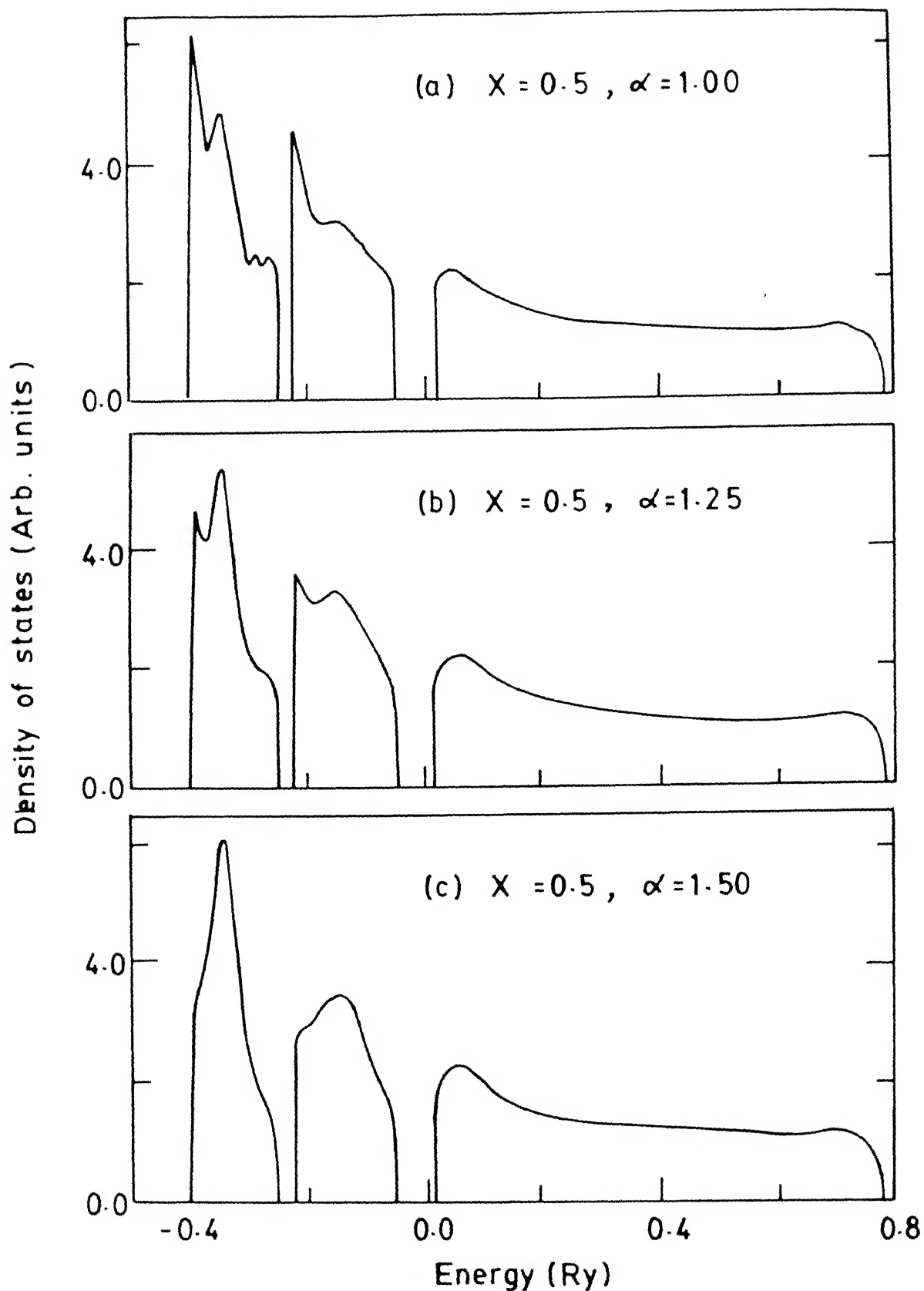Fig. 5.7 Averaged density of states for the alloy with short-range order, for the concentration x = 0.5 by the embedded cluster method of Ref. 50. The short-range order parameters are (a) $\alpha$ = 1.0, (b) $\alpha$ = 1.25, and (c) $\alpha$ = 1.50.
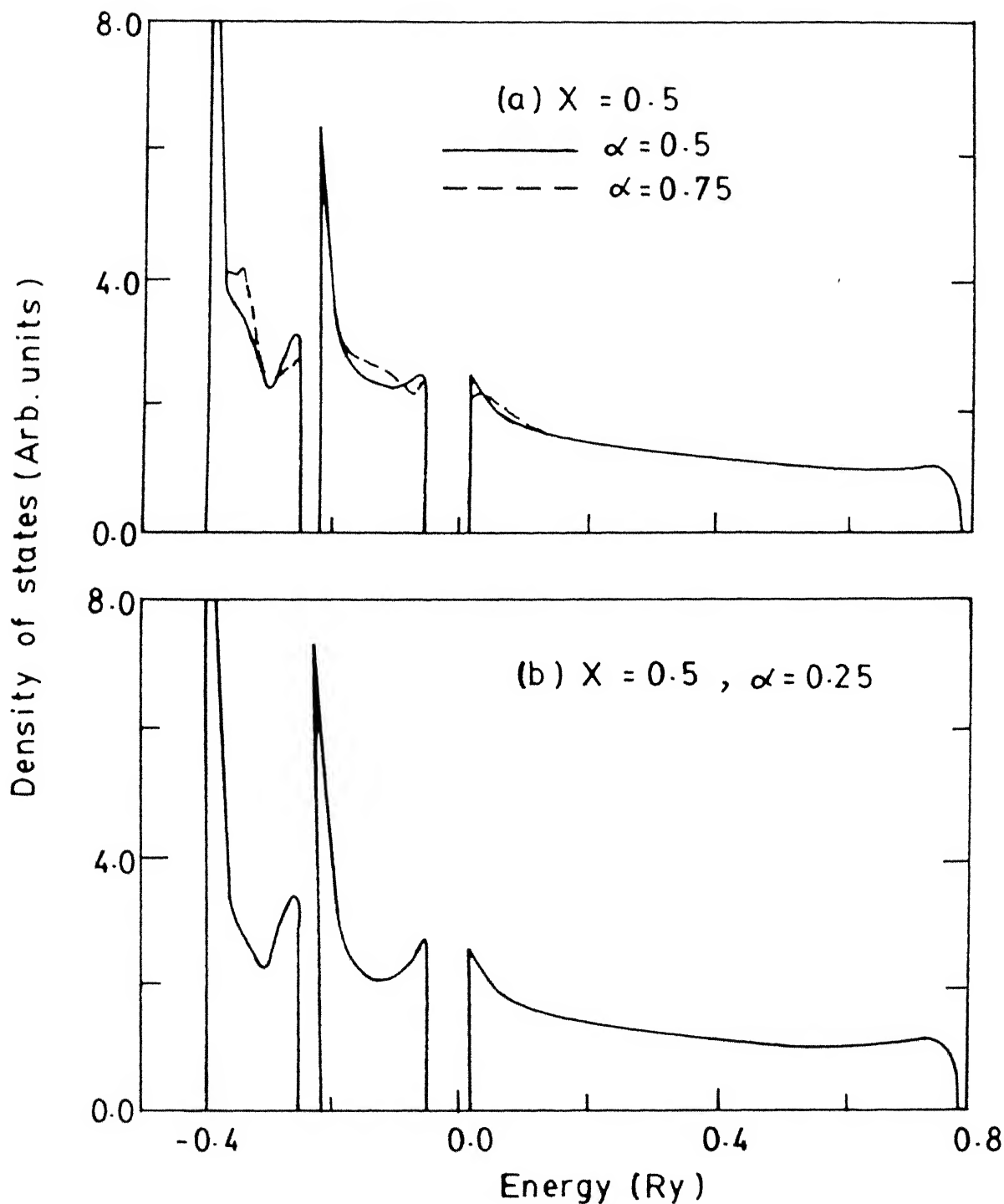
Fig. 5.8 Averaged density of states for the alloy with short-range order, for the concentration x = 0.5 by the embedded cluster method of Ref. 50. The short-range order parameters are (a) $\alpha$ = 0.75 (dashed line), $\alpha$ = 0.50 (solid line), and (b) $\alpha$ = 0.25.

## 5.6 CONCLUSION

In this chapter, we presented the generalization of the configuration averaging process in the augmented space formalism for the systems with short-range order. We used this formalism to determine the configuration average of the site-diagonal form of the KKR Green's function. This averaged Green's function is exact, and therefore, is herglotz. However, for numerical computations, one has to adopt some approximation. This approximation is in addition to the CCPA, which is used to reduce the dimensionality of the augmented space. We calculated the density of states for a one-dimensional muffin-tin alloy with Markovian type short-range order. We found that this approximation yields non-negative density of states for a considerably wide range of values of the short-range order parameter.

# CHAPTER 6
## SUMMARY AND CONCLUSIONS

In this thesis, we discussed a self-consistent cluster generalization of the coherent-potential approximation[3-5] (CPA) for disordered substitutional alloys. This cluster generalization, which is called the cluster coherent-potential approximation[46,58] (CCPA), is developed in the augmented space formalism.[52-55] This approximation includes the correlated scattering from atoms inside a chosen cluster, in a self-consistent way, which may be important in systems showing short-range order and clustering tendencies, such as CuPd, CuPt, and CuNi systems. The augmented space CCPA restores the translational symmetry of the effective medium. In this thesis, we proved three theorems regarding the analyticity of the augmented space CCPA. It was shown that, the augmented space CCPA preserves the analytic (herglotz) properties of the self-energy and the configuration averaged Green's function.[58] Also, it was proved that the self-consistent iteration scheme for the self-energy has a fixed point, i.e. it always converges to a herglotz, unique and bounded value, provided we start off the iteration with a bounded and herglotz one.[58] This guarantees a single-valued, continuous, and non-negative density of states at all energies.

The main objective of this thesis was to present a cluster generalization of the first-principles parameter-free Korringa-Kohn-Rostoker coherent-potential approximation[67,88] (KKR-CPA). We have developed a cluster theory, the KKR-CCPA, by effectively combining the augmented space CCPA and the conventional KKR Green's function formulation of the electronic structure of disordered alloys. The KKR-CCPA formulation has been put on the same footing as the single-site KKR-CPA, in which one can calculate the charge densities, and therefore, can achieve charge self-consistency within the local density approximation of the density functional theory.[13-15] Therefore, our KKR-CCPA formulation can be regarded as a first-principles parameter-free theory of disordered substitutional alloys, in which correlated scattering from clusters of atoms is taken into account. The KKR-CCPA restores the translational symmetry of the effective medium, and like the KKR-CPA, is exact in the limit of vanishing concentration of either constituent. Also, it reduces to the correct limit (KKR-CPA), when we take a one-atom cluster.[67]

The KKR-CCPA formulation was applied to calculate the density of states for a one-dimensional muffin-tin alloy. We found that, the density of states calculated within the KKR-CCPA is more structured[67] compared to the density of states calculated within the single-site KKR-CPA. To understand and investigate the origin of these structures, we

calculated the local density of states on an impurity of different two-impurity clusters embedded in the KKR-CPA medium. We found that, the structures in the KKR-CCPA density of states and those in the local density of states on these impurities were correlated. Also, we compared our results with the averaged density of states of the embedded cluster method of Gonis and coworkers,[59,60] for various cluster-sizes. It was found that, with the increase in the cluster-size the averaged density of states obtained by the embedded cluster method showed more resemblance to the KKR-CCPA density of states. From these observations, it was concluded that, the structures in the KKR-CCPA density of states originate from the correlated scattering from clusters of atoms.[67]

We have formally extended the KKR-CCPA formulation to include non-random effects like the short-range order. We showed that the configuration averaged Green's function in presence of short-range order, can be expanded about that of a purely random system. The correction terms could be expressed in terms of the averaged inverse t-matrices and the configuration averaged Green's function for a purely random system.[70] For numerical computations, we adopted an approximation, in which we truncated the infinite series in the expansion after the first correction term. We applied this formulation to calculate the density of states for the

one-dimensional muffin-tin alloy with Markovian type short-range order.[70] We found that, the density of states remained non-negative throughout the whole energy range, for an appreciably wide range of the values of the short-range order parameter. The density of states became negative at some points, only in the strong short-range order regime. This unphysical behavior is probably due to the breakdown of the approximation, in which the higher order corrections in the expansion of the averaged Green's function are neglected. The contribution of the higher order terms may be significant in the strong short-range order regime. In this regime, the system is closer to an ordered system, rather than a disordered alloy. So, when the alloy is close to an ordered system, it may be more appropriate to expand the averagad Green's function about its value for an ordered system,[99] rather than that of a random system. However, we found that, our approach is successful over an appreciably wide range of short-range order parameters for a one-dimensional model, which is known to be sensitive to any kind of approximation. Therefore, we hope that, our approach will be more successful for a three-dimensional system.

In this work, we have applied the KKR-CCPA formulation to a model case. In principle, this theory can be applied to realistic alloy systems in three dimensions. However, computationally it will be much involved than the KKR-CPA.

But, nevertheless, we feel that, with the availability of the modern computers, the application of the KKR-CCPA to realistic alloy systems can be realized. This problem has been taken up by our group, and we are quite hopeful that, we will be able to report the results within a reasonable time.

We observed sharp structures in the density of states of the one-dimensional muffin-tin alloy calculated within the KKR-CCPA. We expect that, in three dimensions also, the KKR-CCPA will produce sharp structures in the density of states. The appearance of the structures in the averaged density of states may strongly influence some of the physical properties of the alloy. For example, the Fermi energy and the density of states at the Fermi energy are expected to be influenced by the appearance of sharp structures in the density of states, especially, if the structures are in the vicinity of the Fermi energy. Any change in the Fermi energy or the density of states at the Fermi energy, will affect the magnetic and other properties of the alloy. The formation of magnetic moments, the electronic specific heat, superconducting transition temperature, electrical conductivity, Fermi surface etc. are among such properties. The above considerations underline the importance of the KKR-CCPA formulation.

A very important and long sought goal in the theory of disordered alloys is the calculation of phase diagrams[100]

from first-principles. In the determination of phase diagrams by statistical methods, effective pair (and, if necessary, larger cluster) interactions are very important.[101] The effective pair interactions have been so far calculated by embedding two-atom clusters in the KKR-CPA medium,[102] which is a non-self-consistent approach. A better approach would be to use self-consistently calculated effective pair interactions, which come out naturally from our KKR-CCPA approach. Therefore, it is hoped that, our formulation will be helpful in accurate determination of phase diagrams from the first-principles.

The application of the KKR-CCPA formulation to the systems with the tendency to clustering, will be more interesting, especially, in the investigation of those properties which depend intrinsically upon the clustering effects. In CuNi alloy, it is well-known that, Ni atoms will carry a magnetic moment only if surrounded by a sufficiently large number of other Ni atoms.[16,17] In CuPd system, the density of states calculated within the KKR-CPA (Refs. 23 and 24) does not agree with the experimental results,[26] especially in the lower energy region.[27] Many systems like CuPt and CuPd are known to have short-range ordering. These systems are, therefore, ideal systems for the application of the KKR-CCPA.

One problem which needs further work, is the embedding of a cluster of real atoms in the KKR-CCPA effective medium. The KKR-CCPA, quite predictably, introduces site-off-diagonal corrections as well in the inverse effective t-matrices, along with the usual site-diagonal corrections. The off-diagonal corrections in the t-matrices are quite complicated and their dependence on the potentials of the two involved sites is not explicitly known. This poses problem in determining the off-diagonal term between a real atom and an effective atom, when a cluster of real impurities is embedded in the effective medium. Though, we found that, the basic structure of the local density of states on the impurities is almost independent of different choices of the off-diagonal terms,[67] we feel that, this problem requires some attention.

The study of topologically (structurally) disordered alloys is largely untouched. The KKR-CCPA formulation presented in the present thesis also, is valid only for substitutionally disordered alloys. In most of the systems, especially in liquid alloys and amorphous solids, topological disorder is coupled with strong short-range order.[103] Some of the well-known theories for liquid alloys are, the liquid CPA,[104] the effective medium approximation,[105,106] the methods of Schwartz and Ehrenreich,[107] Györffy,[108] and Korringa and Mills.[109] None of these theories are proved to

lead to a herglotz Green's function, and analyticity difficulties and convergence problems show up in calculations.[110] We have tackled the problem of short-range order to some extent in this thesis. It will be interesting to generalize this formulation for systems with topological disorder.

Our KKR-CCPA formulation is a non-relativistic theory. For disordered alloys containing heavy elements (like 5d elements), the relativistic effects are expected to be important. A fully relativistic version of the single-site KKR-CPA and its successful application to many systems have been reported in the literature.[87] Very recently, it even became possible to develop a cluster generalization of the relativistic KKR-CPA in the embedded cluster method.[111] The relativistic KKR-CPA embedded cluster method, in essence, is a combination of the relativistic KKR-CPA of Staunton $et$ $al$[87] and the embedded cluster method of Gonis and coworkers.[50,60] This has been very successful in predicting the short-range order effects in CuPt (Ref. 112) systems. But, nevertheless, this remains a non-self-consistent approach. A self-consistent cluster generalization of the relativistic KKR-CPA may be realized, if one can efficiently apply the augmented space formalism to this problem.

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